ENVIRONMENTALLY SUSTAINABLE MINING: REUSABLE ZEOLITES FOR SODIUM MITIGATION FROM POTASH BRINE IMPACTED GROUNDWATER

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Abstract

Potash mining creates highly saline waste products. Current industry standards include storage and contamination prevention measures; however, the risk to surrounding soil and groundwater from the highly saline waste solution is a significant concern.

Zeolites, specifically clinoptilolite-rich zeolites, have drawn significant attention as a viable and cost-effective treatment method for contaminated solutions. Zeolite has been successful in the reclamation of saline coalbed natural gas co-produced solutions; however, zeolites have thus far not been specifically examined for desalination of potash brine impacted solutions. The desalination capabilities of three natural zeolites from mines located in North America, were examined using synthetic saline solutions and groundwater spiked with potash brine from a local Saskatchewan mine. Bear River zeolite (Idaho, USA) was the most effective, achieving a Na^+ removal percentage of approximately 70%. A selectivity sequence of $K^+ > Na^+ > Ca^{2+} \approx Mg^{2+}$ was determined through batch adsorption experiments with potash brine spiked groundwater.

Pre-treatment strategies were evaluated during this study to optimize the adsorption capacity of the natural zeolites. Acid treatment (1M H_2SO_4) was used to promote protonation of the zeolite exchange sites, resulting in an increase Na^+ sorption capacity of approximately 10%. However, the sorption solution was strongly acidic and problematic for practical applications. Cations such as sodium and calcium have commonly been used to pre-treat zeolites to increase the sorption capacity. As sodium removal was the primary objective, thus, pre-treatment techniques using calcium and magnesium ions were examined. A hard water solution was simulated using $CaCl_2$ and $MgCl_2$ to remove the Na^+ ions from zeolite exchange sites. This technique increased the Na^+ removal percentage for the Canadian zeolite by approximately 77%.

Sodium sorption experiments created zeolite with sodium saturated exchange sites. To minimize the waste products produced, this study examined sodium removal and water softening cycles. The significant Na^+ sorption improvement suggested initially using the Canadian zeolite to soften simulated hard water, producing Ca- and Mg-rich zeolites and recycling the zeolite for Na^+ adsorption experiments. The dual treatment of saline and hard water solutions was studied for five complete cycles with a stable functioning exchange system being achieved. The regeneration increased sorption capacity while extending the life cycle of the zeolite adsorbent.

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Abbreviations and Symbols

*	Significance level of $p \leq 0.05$ (95% confidence interval)
**	Significance level of $p \leq 0.01$
***	Significance level of $p \leq 0.001$
****	Significance level of $p \leq 0.0001$
A	Activity of soil
Å	Angstrom
AIC	Araike's Information Criterion
Al^{3+}	Aluminum
Al-O-Si	Aluminum, oxygen and silica bonds
ANOVA	Analysis of variance
BC	British Columbia, Canada
BET-N_2	Brunauer-Emmett-Teller nitrogen method for surface area
BR	Bear River Company
BRZ	Natural Bear River zeolite
BRZ(0.1M)	0.1M H_2SO_4 treated Bear River zeolite
BRZ(1M)	1M H_2SO_4 treated Bear River zeolite
BRZ(2M)	2M H_2SO_4 treated Bear River zeolite
C_0	Initial concentration in solution (mg/L or meq/L)
Ca^{2+}	Calcium
Ca^{2+}/Mg^{2+}	Synthetic hard water solution
Ca^{2+}/Mg^{2+}–BRZ	BRZ after undergoing batch adsorption with Ca^{2+}/Mg^{2+} solution
Ca^{2+}/Mg^{2+}–CMZ	CMZ after undergoing batch adsorption with Ca^{2+}/Mg^{2+} solution
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
C_e	Equilibrium concentration (mg/L or meq/L)
CEC	Cation exchange capacity in milliequivalents per 100g of soil (meq/100g)
CM	Canadian Mining Company
CMZ	Natural Canadian Mining zeolite
DI	Deionized water

ECEC	Effective cation exchange capacity
EDTA	Ethylenediamine Tetraacetic acid
H^+	Hydron ion
H_2SO_4	Sulphuric acid
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
I_P	Plasticity index of soil
K^+	Potassium
KCl	Potassium chloride
K_F	Freundlich constant
K_L	Langmuir Coefficient
kPa	Kilopascal
M	Molarity
m	Mass of adsorbent in grams (g)
m/V	Mass (g) to volume (L)
meq/L	Milliequivalents per litre
mg/L	Milligram per litre
Mg^{2+}	Magnesium
$MgCl_2$	Magnesium chloride
n	Freundlich exponent
Na^+	Sodium
Na^+–BRZ	BRZ after undergoing batch adsorption with Na^+ solution
Na^+–CMZ	CMZ after undergoing batch adsorption with Na^+ solution
NaCl	Sodium chloride
NH^{4+}	Ammonium
NH_4OAc	Ammonium acetate
PB+GW	Potash brine and groundwater solution
PB+GW(500)	Potash brine and groundwater mixed to create a Na^+ concentration in solution of approximately 500 mg/L (21.75 meq/L)
q	Mass solute adsorbed (mg/g)
q_e	Maximum adsorption capacity (mg/g)

R^2	Coefficient of determination
RO	Reverse osmosis
rpm	Revolutions per minute
SAR	Sodium adsorption ratio
SCZ	Natural St. Cloud zeolite
SEM	Scanning electron microscope
Si/Al	Ratio of silica to aluminum in the zeolite framework
Si^{4+}	Silica ion
SRC	Saskatchewan Research Council
STXM	Scanning transmission x-ray microscope
TCEC	Total cation exchange capacity
USA	United States of America
V	Volume in litres (L) or millilitres (mL)
w_L	Liquid limit of soil
w_p	Plastic limit of soil (plasticity)
XRD	X-ray Diffractometer
XRF	X-ray Fluorescence

1 – General Introduction

Potash mining is one of the primary industries supporting Saskatchewan's economy. It is estimated that Saskatchewan produces approximately one third of the world's potash supply (SMA, 2012; Rawashdeh and Maxwell, 2014). Mining potash, or sylvite, produces waste in the form of salt tailings and a brine solution. The tailings are composed of approximately 90% sodium chloride (NaCl), 7-8% potassium chloride (KCl) and trace amounts of insolubles such as clay minerals or dolomite (Wong and Barbour, 1987). In 1990, ten potash mines were operating at capacity in Saskatchewan, producing approximately 2.8×10^7 tonnes of tailings which resulted in 1.1×10^7 m^3 of brine annually (Tallin et al., 1990). It is important to note that these levels have and will continue to increase along with product demand and capacity expansions (Rawashdeh et al., 2016). The brine is of significant concern as it is highly saline and more difficult to contain than solid tailings (Reid and Getzlaf, 2004). The brine is typically stored on site, in a lined storage pond. In Saskatchewan, these mine waste storage ponds often overlay freshwater aquifer systems so infiltration of the highly saline solution into underlying sediments and subsequent aquifers is a major environmental concern. Groundwater systems are complex and source contamination could become a widespread issue. Majority of potash mines in the province are also surrounded by agriculture land. This means that brine infiltration could have a major impact on surrounding ecosystems as high sodium levels in soils can impact physical and chemical soil properties such as its permeability, aggregate stability and soil infiltration (Seelig et al., 1990; Mohamed et al., 2005). Saline groundwater and soils can significantly impact the environment, as well as be detrimental to local economies such as Saskatchewan that depend on agriculture; by changing the soil structure, the presence of sodium impairs water infiltration which negatively affects plant growth.

Current industry practices to manage potash waste is to create a slurry solution using salt water from the brine pond to pump the waste to a tailings management area. The coarse tailings are deposited using a spigot onto the slope of the tailings pile where the saturated solution (brine) drains through and out of the underlying engineered drainage system to be reused as a slurry solution or to the brine pond (Hart, 1989). Fine tailings are deposited in storage ponds located at the lowest elevation on site to encourage drainage of other solutions, such as rainfall, into the tailings ponds. They have traditionally been constructed of compacted clays and tills and potash

mines have more recently began using commercialized high-density polyethylene liners to limit brine seepage (MDH Engineered Solutions, 2009). If geological conditions permit, surplus brine is disposed of through injection wells into underlying formations with naturally high salt contents (Reid, 1984; Thorpe and Neal, 1991). Dykes, slurry walls and interception ditches are common brine and tailings control structures to limit migration offsite (Vonhof, 1975). Monitoring plans are also in place to monitor potential brine migration so remedial action can be implemented. Immediate remedial action has always been an issue for many mining industries. Current desalination methods for many industries include 'pump and treat' systems using conventional and costly water treatment techniques such as reverse osmosis, infiltration ponds, subsurface drip irrigation and ion exchange (Chen et al., 2011; Santiago et al., 2016). Thus, a cost-effective desalination method is needed.

1.1 Research Significance

Using zeolite as an adsorbent for water treatment purposes has gained popularity over the past decade; however, minimal research has been conducted on its potential to remove sodium. Saskatchewan is a world leader in potash mining but the current waste management practices within this industry do not commonly include active remediation (Huang and Natrajan, 2006). Mines are surrounded by agriculture land where saline contamination of groundwater and soil could be detrimental. The waste storage facilities on potash mines often overlay aquifers and as these mines expand to accommodate a growing demand, the potential infiltration area grows and thus does the risk (Vonhof, 1975). Having a remedial option will help alleviate some of the stigma associated with property in close proximity to these facilities as well as address possible downstream contaminant migration and contamination.

Current environmental regulations in Saskatchewan are ensuring mining companies think towards the future and how to manage waste products; as of 2004, no potash mine in the world had been successfully decommissioned and reclaimed to an environmental standard which would be acceptable in Saskatchewan (Reid and Getzlaf, 2004). Zeolite has been proven to be successful at removing sodium from coalbed produced waters (Taulis and Milke, 2007; Zhao et al., 2008; Millar et al., 2016) but the proposed zeolite types and their interaction with potash waste samples has never been investigated. A few studies have been published on the use of acid activation techniques

to modify the zeolite in order to increase its adsorption potential; however, they were focused on sodium concentrations less than practical for potash applications. A study evaluated an Australian zeolite and found that it increased the sodium adsorption capacity by almost four times over natural; however, this experiment only used sodium concentrations less than 600 mg/L (Wang et al., 2012). Therefore, it was important to evaluate the sorption potential of acid treated zeolites at higher initial sodium concentrations.

The practical application of using zeolite for engineering purposes has not been widely observed in published literature. Minimal research has been conducted on the hydraulic conductivity of zeolite, with majority only experimenting with bentonite-zeolite mixtures (Kayabali, 1997; Oren et al., 2011). In order to widen the list of potential future uses for the zeolite, this study investigated zeolite hydraulic conductivity and sorption influencing properties. This will allow industry to select the optimum material, based on level of modification, type of zeolite and sorption conditions for the intended use.

Traditional pre-treatment and regeneration techniques for sodium ion exchange includes stripping the sodium from exchange sites using calcium (Capasso et al., 2007; Stefanović et al., 2007; Gedik and Imamoglu, 2008). This method requires creating a concentrated calcium solution and disposal of the waste effluent product. An alternative option would be to recycle the zeolite for hard water treatment. Creating sodium removal and water softening cycles would produce a smaller waste product and most importantly, increase the lifecycle of the zeolite. A few studies have evaluated the potential for zeolite as a water softening technique but only one has created cycles with sodium removal using natural sodium rich zeolite (Zhao et al., 2009). This study investigated the pre-treatment and regeneration potential for zeolite adsorbents for their combined use for sodium removal and hard water treatment. Multiple zeolites were studied to determine the influence naturally abundant exchangeable cations have on regeneration potential.

1.2 Research Objectives

The primary objective of the intended research study was to evaluate multiple natural and acid treated zeolite adsorbents for sodium removal, for their potential use within the potash industry. The sodium uptake was measured from synthetic sodium solutions and simulated conditions using potash brine and groundwater mixtures. The zeolites were analyzed for their sorption properties

and hydraulic conductivity; these characteristics will be useful to distinguish the practicality of each zeolite for potential future applications. Acid modification was used in an attempt to optimize the sodium adsorption capacity. The life cycle of the spent zeolite will be further extended through regeneration of the homoionic zeolite using sodium and hard water solutions to create alternating treatment cycles.

This study was separated into two chapters containing experimental methods, results and analysis to research the following objectives:

1. Determine the zeolite characteristics influencing ion exchange, as well as the hydraulic conductivity, to aid in evaluating future applications.
2. Chapter 2: Sodium Sorption from Potash Brine Impacted Groundwater
   a) Evaluating the sodium sorption potential of multiple natural and acid treated zeolites.
   b) Investigate the sodium removal from simulated potash brine impacted groundwater.
3. Chapter 3: Integrated Treatment Process of Sodium Sorption and Water Softening Cycles
   a) Evaluate the influence of pre-treatment using calcium and magnesium, or sodium, on zeolite sorption potential.
   b) Expand the spent zeolite lifecycle through sodium sorption and water softening cycles.

1.3 Scope

The scope of this M.Sc. research was limited to exploring the potential of the proposed zeolite-based remediation prototype for salinity mitigation of potash brine impacted groundwater. This study attempted to elucidate the mechanisms associated with ion exchange, adsorption, modification, and regeneration at a lab scale. Zeolite was the only adsorbent evaluated and the effects of the natural variability of zeolites was not considered within the scope of this study. The field implementation of the material was not determined, rather the results from the study can be used in the future to assist in choosing the optimum material based on the intended use.

The scope included evaluating the maximum adsorption capacity of sodium using agitated batch experiments with natural, acid treated and pre-treated zeolites. A kinetic study using column analysis was not investigated during this study. A waste management method for the acid waste from modification procedures was not created. Experiments were conducted using either synthetic

sodium or hard water solutions and potash brine and groundwater samples to simulate potential practical conditions. The chemical analysis of compounds associated with potash brine impacted groundwater was limited to those cations suspected to be influencing sodium sorption. No numerical analysis was conducted; however, a basic statistical analysis of the laboratory results was completed using a statistical computation program.

The evaluated properties researched focused on those suspected to be influencing sorption, as well as the particle size distribution, consistency limits, index properties and hydraulic conductivity. Some of the sorption influencing properties were tested externally with analysis provided by the authors of this study, where necessary.

2 – Sodium Sorption from potash brine impacted groundwater using natural and engineered zeolites [1]

[1] This chapter is written in joint authorship with Dr. Wonjae Chang (academic supervisor) and James Dynes. James Dynes completed and analyzed STXM data on some of the zeolite absorbents researched in this study. The STXM analysis was completed at the Canadian Light Source. All other data analysis, examination, as well as manuscript preparation, was completed by Ashley Siemens under the direct supervision of Dr. Wonjae Chang. Dr. Wonjae Chang is the Principal Investigator of the IMII research program in which this study is a part of.

2.1 Abstract

The effectiveness of using natural and engineered zeolites for the reclamation of saline water produced during coalbed methane developments has drawn significant attention to zeolites as cost-effective remedial materials in the United States of America (USA) and Australia. Thus far, natural zeolites have not been specifically examined in the context of sodium salinity mitigation for mining-impacted solutions in Canada. This study aims at investigating the use of natural and acid treated zeolites for the remediation of groundwater impacted by highly saline mine effluents (potash liquid brine). Natural zeolites from British Columbia, Canada and New Mexico and Idaho, USA and acid treated zeolites (conventional acid activation), were tested for their capability to desalinate synthetic saline water and groundwater spiked with brine solution from a Saskatchewan potash mine. Bear River zeolite (Idaho, USA) achieved the highest Na^+ removal percentage of the natural adsorbents studied, with 70% Na^+ removed. Acid treating natural zeolites with 1M H_2SO_4 increased the sodium removal by approximately 10%; however it generated strongly acidic sorption solutions, which is problematic in practice. Adsorption experiments using groundwater spiked with potash brine provided insight on the zeolite's natural selectivity (K^+>Na^+>Ca^{2+}=Mg^{2+}). The presence of additional cations in the PB+GW solution lowered the Na^+ removal by approximately 10%.

2.1.1 Keywords

Zeolite, clinoptilolite, sorption, ion exchange, sodium removal, potash brine impacted groundwater, acid treatment

2.2 Introduction

The mining of potash, or sylvinite, plays a vital role in sustaining the world's food supply by providing nutrients, in the form of fertilizer, to promote plant growth (Marshall, 2015). Canada leads the world in potash ore reserves and production, with approximately half of the world's potash reserves located in Canada (SMA, 2012; Marshall, 2015). The sylvinite ore varies depending on deposits but commonly contains approximately 30-40% sylvite or potassium chloride (KCl), 50-70% halite or sodium chloride (NaCl) and 1-8% insolubles (Vonhof, 1975; Reid and Getzlaf, 2004). Potash mining waste primarily consists of NaCl (approximately 90%), 7-8% KCl and trace amounts of insolubles such as clay minerals or dolomite (Wong and Barbour, 1987). The highly saline waste forms solid salt tailings and highly concentrated liquid brine. Improved mining and refining methods have reduced the production of potash mine wastes over time; for every tonne (t) of KCl refined, the mass of tailings produced improved from approximately 2 to 2.5 t prior to mid-1980 (Wong and Barbour, 1987; Tallin et al., 1990), to less than 0.5 t in the past decade, with brine production rates near 0.2 t (PotashCorp, 2011; Mosaic, 2015). Although the volume of salt waste produced has decreased with improved mining and refining techniques, production rates have increased over time, thus, increasing the total amount of waste produced annually. Tailings are transferred to the waste management area in a slurry and deposited onto the tailings pile, where liquid brine infiltrates and flows into the brine ponds surrounding the tailings pile. The brine is recycled into the mining process, with excess disposed through deep well injection into saline aquifers, or natural evaporation and a small portion remaining in the ponds as residual moisture (Reid, 1984; Thorpe and Neal, 1991; Reid and Getzlaf, 2004). The leakage of saline potash brine into surrounding soil and water ecosystems is a significant environmental concern, thus, designing a sufficient waste management system is a priority. Passive or active containment measures offer secondary containment options to the lined brine pond. The extensively engineered systems are designed to minimize the risk of contaminant migration and consist of dykes, impoundment walls, trenches, drainage ditches and capture wells (Hart, 1989).

Significant effort is made to minimize the migration of saline brine solutions; however, liquid is extremely difficult to contain and some level of contamination is deemed inevitable (Hart, 1989; Thorpe and Neal, 1991). The long term exposure of soil to saline waters deteriorates physical soil

properties, ultimately negatively impacting plant growth (Seelig, 2000). Soil salinity describes an increased concentration of salt in the soil (Mau and Porporato, 2015); this is commonly described by the sodium adsorption ratio (SAR), which is a measure of the tendency of sodium (Na^+) ions to be adsorbed at the expense of magnesium (Mg^{2+}) and/or calcium (Ca^{2+}) cations (Bernstein, 1975):

$$SAR = \frac{[Na^+]\ (meq)}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]\ (meq)}{2}}} \tag{2.1}$$

Soil exposure to high sodium levels deflocculates soils leading to soil dispersion which causes reduced soil permeability, thus, reducing water infiltration required for plant growth (Warrence et al., 2003) as well as increasing the susceptibility to wind and water erosion (Daliakopoulos et al., 2016). High salt levels also alter the osmotic pressure of the water, thus, reducing the plant's water availability and leading to nutrient imbalances and physiological drought (Agriculture, 2008; Mau and Porporato, 2015). Salinity contamination not only impacts agriculture production and environmental soil and water quality, it can evolve into social and economic loss (Daliakopoulos et al., 2016), therefore, it is vital to find salinity remediation alternatives that are healthy for the environment and economically viable. Active desalination techniques commonly include multistage flash, reverse osmosis, electrodialysis or ion exchange technologies (Wajima et al., 2010). It has been noted that although effective, desalination methods such as reverse osmosis have high operating and capital costs (Chen et al., 2011; Santiago et al., 2016), therefore the cost effectiveness of ion exchange technologies utilizing zeolite has begun to gain popularity for salinity remediation purposes in the areas of desalination of sea water (Wajima et al., 2010; Wajima, 2013) and co-produced natural gas waters (Taulis and Milke, 2007; Ghaly and Verma, 2008; Zhao et al., 2009; Belbase et al., 2013; Millar et al., 2016).

Natural zeolites are crystalline, hydrated aluminosilicates of alkaline and alkaline earth elements; the silica (Si^4) and aluminum (Al^{3+}) atoms are bound by covalent bonds over shared oxygen atoms (Sprynskyy et al., 2005; Lei et al., 2008; Chen et al., 2014; Ebrazi and Banihabib, 2015). The rigid, three dimensional framework is free from the shrink swell behavior common to other clay types (Bowman, 2003). Zeolites are present in natural deposits, typically hydrothermally altered volcanic or sedimentary rocks (Vala Ragnarsdottir et al., 1996). Zeolite is mined in a solid rock form using a conventional open pit mining method (Virta, 1997). The most common natural zeolite forms are clinoptilolite, erionite, chabazite, mordenite and phillipsite (Widiastuti et al., 2011).

Chabazite and clinoptilolite deposits are mined in USA and Canada with chabazite deposits located in Nevada and Arizona USA (Virta and Phamdang, 2002) as well as Nova Scotia, Canada (Pe-Piper and Miller, 2003). Clinoptilolite is mined in British Columbia (BC), Canada (Read, 1995) as well as six states is the USA: California, Idaho, New Mexico, Oregon, Texas (Virta and Phamdang, 2002). Clinoptilolite is a sedimentary zeolite species (Yukselen-Aksoy, 2010) and one of the most predominant due to its ion exchange properties, eco-friendly nature, low cost and abundance worldwide (Cui et al., 2006; Delkash et al., 2015).

The zeolite structure has a negative surface charge from the isomorphic substitution of Si^{4+} for Al^{3+}; this charge is balanced by positively charged exchangeable cations, such as Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} (Chen et al., 2014; Ebrazi and Banihabib, 2015). This property promotes the exchange of cations between a liquid phase and those being held on the zeolite framework by electrostatic forces (Ghaly and Verma, 2008). The diffusion of cations is a result of a concentration gradient between the solid and liquid phases which exists until ion exchange reaches equilibrium state. The cation exchange capacity outlines the number of ions which can be adsorbed or exchanged resulting from the replacement of Si^{4+} for Al^{3+} and presence of cations balancing the resulting negative charge on the zeolite framework (Erdem et al., 2004). The cation exchange capacity (CEC) of clinoptilolite-rich zeolites ranges from 60meq/100g to 230meq/100g (Wang and Peng, 2010). The adsorption behavior (selectivity and capacity) depends on: the valence charge, field strength and hydration degree of the cation (Cui et al., 2006); surface area, accessibility of exchange sites, cation exchange capacity, mineral purity and natural silica to aluminum (Si/Al) ratio of the zeolite (Inglezakis et al., 2001; Cheng et al., 2005) ; and experimental properties including initial ion concentration, solid to liquid ratio, presence of competitive ions, and contact time (Wang and Peng, 2010; Delkash et al., 2015). The zeolite framework tends to have a higher affinity for monovalent over divalent cations (Mumpton, 1999; Misaelides, 2011). Cations with the same valence are generally selectively exchanged based on the field strength of the cation; cations with low hydration energy are generally preferred and selectively exchanged by the clinoptilolite (Inglezakis et al., 2003; Dyer and Emms, 2005). Clinoptilolite's suggested selectivity sequence is: $Cs>Rb>K>NH_4^{+}>Ba>Sr^{2+}>Na^{+}>Ca^{2+}>Fe^{3+}>Al^{3+}>Mg^{2+}>Li^{+}$ (Cooney et al., 1999; Mumpton, 1999; Liu and Lo, 2001). The suggested selectivity preference of Na^{+} over Ca^{2+} of clinoptilolite-rich zeolites shows promise; however, some previous studies have also suggested preference for Ca^{2+} (Curkovic et al., 1996; Inglezakis, 2005; Park et al., 2007; Seo et al., 2010; Xu

et al., 2012). The zeolite's open framework has an extensive system of interconnected channels and voids, acting as a molecular sieve by allowing ions to exchange depending on the hydrated radii of the cation and channel size and configuration, as well as cation charge and concentration (Oren and Kaya, 2006). The porous structure and extensive channel network results in a large specific surface area which contributes to an increased exchange capacity (Öztaş et al., 2008; Vivacqua et al., 2013). Zeolites also possess desirable catalytic, hydraulic, mechanical and thermal properties (Misaelides, 2011), as well as being eco-friendly and chemically stable in high temperature, acidic and corrosive environments (Ji et al., 2007; Xue et al., 2014).

The unique sorption and selectivity properties of zeolites has promoted their use as an ion exchange media in many applications. Zeolites were successfully used in wastewater treatment, agronomy, horticulture, aquaculture, nuclear waste treatment and multiple other industries (Cui et al., 2006; Wajima, 2013). The non-toxic nature of the exchangeable alkaline and alkaline earth cations, allow for an environmentally friendly water treatment alternative (Panayotova, 2001; Gaikwad et al., 2011; Tomić et al., 2012). The use of natural and acid treated zeolites (predominately clinoptilolite) to improve water quality has been thoroughly investigated for the removal of ammonium (Cooney et al., 1999; Bolan et al., 2003; Liang and Ni, 2009; Fu et al., 2011) and heavy metal ions such as Pb^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Cd^{2+}, Cu^{2+} and Cr^{2+} (Inglezakis et al., 2002; Wingenfelder et al., 2005; Oter and Akcay, 2007; Öztaş et al., 2008; Wang and Peng, 2010). The low technology requirements associated with zeolite ion exchange systems, combined with the inexpensive cost to mine and produce zeolite (Widiastuti et al., 2011), promotes it as an economically viable remediation alternative. Clinoptilolite-rich zeolites have also been used for salinity mitigation from soil and compost (Wajima et al., 2010), as well as natural gas co-produced waters, in Australia and Wyoming, USA; the majority of these studies focused primarily on synthetic sodium solutions with low initial concentrations (Zhao et al., 2008; Zhao et al., 2009; Ganjegunte et al., 2011).

Physical or chemical modification techniques have been used to alter adsorption properties, thus, aiming to increase the exchange capacity of the zeolite (Klieve and Semmens, 1980; Liang and Ni, 2009). Chemical modification commonly occurs using cationic surfactant, alkali earth metals and acids. Cationic surfactants create surfactant modified zeolites which are capable of exchange reactions with cations (Cortés-Martínez et al., 2004), anions (Ghiaci et al., 2004) and organic compounds (Bowman, 2003). Chemical treatment using alkali earth metals or acids increases the

content of a more easily removable cation through the replacement of those pre-existing on exchange sites, creating a near homoionic condition on the zeolite framework (Panayotova and Velikov, 2003; Gorimbo et al., 2014). Previous studies commonly used ion exchange with NaCl to create homoionic ion exchange conditions (Sprynskyy et al., 2005; Lei et al., 2008); as Na^+ uptake is the purpose of this study, pre-treatment using an acid solution was studied. Acid treated clinoptilolite has been studied for the removal of sodium (Wang et al., 2012; Santiago et al., 2016), ammonium (Bolan et al., 2003; Fu et al., 2011; Li et al., 2011) and heavy metals (Günay et al., 2007; Gedik and Imamoglu, 2008; Li et al., 2008; Xu et al., 2014). During acid treatment, the protons attack the Al-O-Si bonds which weakens the framework and causes cracks, defects and vacancies (Jozefaciuk, 2002). The framework damage causes an enlarged pore network, thus, increasing the zeolite's micropore volume and surface area (Li et al., 2011). Aluminum ions become available to be leached from the framework through dealumination or the breaking of Al-O bonds (Christidis et al., 2003; Garcia-Basabe et al., 2010). The structural implications of zeolite dealumination have been inconsistent in previous studies; however, majority suggested a strong influence of the Si/Al ratio, with stronger acid-resistivity for those zeolites with higher silica contents such as clinoptilolite (Salvestrini et al., 2010; Wang et al., 2016). A study completed by Xiaoyu Wang and associates (2012) for the removal of sodium from coalbed natural gas produced water using natural and acid treated Australian clinoptilolite-rich zeolites. In this study, acid (0.1M H_2SO_4) modification of natural zeolite increased the sodium uptake by almost 50%; however initial concentrations above approximately 600 mg/L Na^+ were not evaluated (Wang et al., 2012).

Numerous publications have reported the use of zeolite for water treatment; however, there have been few evaluating the use of zeolite as a candidate for permeable reactive barriers and landfill liners (Oren et al., 2011). Clay minerals typically have low permeability which leads to poor drainage and good hydraulic containment (Lade, 2001). The hydraulic conductivities of clays can be substantially different depending on mineral composition (Kayabali, 1997) and weathering or fracturing (Lade, 2001), as well as density, porosity, void ratio and grain size distribution of the clay (Hunt, 2005a). Previous studies evaluating the permeability of zeolites has been mainly limited to Turkish zeolites (Tuncan et al., 2003; Yukselen-Aksoy, 2010; Oren and Ozdamar, 2013). Currently, only a single study was found that combined the determination of zeolite hydraulic conductivity and the ion exchange capacity; this study focused on heavy metal ions, primarily

copper (Turan and Ergun, 2009). The hydraulic conductivity will be an important property when evaluating the zeolite's viability for future remedial applications.

This study aims at evaluating three natural clinoptilolite-rich zeolites for their salinity mitigation potential based on sodium removal rates and zeolite characteristics. Characterizing zeolite samples is important for analyzing their sorption performance as well as predicting future engineering behavior. Physiochemical properties were determined to assist in evaluating the engineering and adsorption behavior. These properties include particle size, mineral and chemical compositions, cation exchange capacity, exchangeable ions, consistency limits and hydraulic conductivity.

Batch adsorption experiments were conducted with three North American zeolites (in their natural and acid treated forms), over a wide range of initial sodium (Na^+) concentrations with synthetic saline solutions and simulated potash brine impacted groundwater. Previous studies using these North American zeolites primarily focused on heavy metal ion exchange (Wingenfelder et al., 2005; Oter and Akcay, 2007; Vivacqua et al., 2013) or sodium removal from coal bed natural gas produced waters which tended to focus on lower Na^+ concentrations than desired for potash brine impacted waters (Zhao et al., 2009; Ganjegunte et al., 2011; Millar et al., 2016). Batch adsorption experiments were useful for evaluating the Na^+ adsorption potential, including exposure to alternative cations competing for exchange sites, as well as the selectivity of the natural zeolite for primary cations. The selectivity sequence, primarily the preference of zeolite for K^+ ions (Cooney et al., 1999; Sprynskyy et al., 2005; Fu et al., 2011), and the known composition K^+ ions in potash brine, reinforced the need to evaluate the effectiveness of the zeolite for sodium uptake from synthetic and potash brine impacted groundwater.

2.3 Materials and Methods

2.3.1 Material Characterization

Adsorption experiments in this study are divided into two categories based on initial sodium solution: synthetic (analytical grade sodium chloride) and potash brine spiked groundwater (PB+GW). The initial Na^+ concentration range of the synthetic solutions was 250-10,000 mg/L. The potash liquid brine was acquired from a fine tailings pond at a mine in Saskatchewan. The groundwater sample was drawn from a rural drinking well located northwest of Saskatoon, SK.

Potash brine was mixed with groundwater at varying v/v ratios to create designated initial sodium concentrations of approximately 500, 1,000, 2,000, 5,000 and 10,000 mg/L Na^+. The cation chemistry of the potash brine, groundwater and potash brine spiked groundwater with an initial Na^+ concentration of 500 mg/L (PB+GW(500)), was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES).

Zeolite was acquired from St. Cloud Zeolite Co. (Winston, New Mexico, USA) and Bear River Zeolite Company Inc. (Preston, Idaho, USA). The Bear River (BRZ) and St. Cloud (SCZ) zeolites were selected based on previously reported sorption performance (Bowman, 2003; Zhao et al., 2008; Ganjegunte et al., 2011; Xu et al., 2012). The Canadian Mining Zeolite Company (Vancouver, British Columbia) supplied zeolite tuff (CMZ) from their Bromley Creek Mine (Princeton, British Columbia). Zeolite tuffs were pulverized (Bico UA disk pulveriser), producing powdered zeolites which were analyzed for particle size distribution (Malvern Mastersizer 2000). A particle size distribution analysis was performed on natural (BRZ, CMZ and SCZ) and acid (1M H_2SO_4) treated zeolites (BRZ(1M)). The mineralogical content of the zeolite samples was determined from x-ray powder diffraction patterns using a Bruker D4 Endeavor X-ray Diffractometer (XRD) with Cu Kα radiation at 1.54 Å. An elemental analysis was performed on the samples by X-ray Fluorescence (XRF) Spectroscopy (Bruker S8 TIGER). Zeolite specific surface area was measured using the Micromeritics ASAP2020 nitrogen (N_2) adsorption method; samples were degassed for two hours at 150°C prior to analysis. The Brunauer-Emmett-Teller (BET) formula calculated the specific surface area from nitrogen isotherms at 77 K.

An ammonium acetate method (Hendershot et al., 2007) was used at a neutral pH to determine both exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and CEC. The exchangeable cations were removed using a 1M ammonium acetate (NH_4OAc) sorbate solution and measured using ICP-OES. The summation of the exchangeable ions correlates to the effective cation exchange capacity (ECEC) (Hendershot et al., 2007; Ganjegunte et al., 2011). The total cation exchange capacity (TCEC) was determined by measuring the concentration of the ammonium (NH_4^+) cations displaced by a concentrated solution containing a second cation with near equal selectivity preference (Hendershot et al., 2007). A potassium chloride solution (1M KCl) was introduced to exchange with ammonium (NH_4^+) ions and the TCEC was calculated using a mass balance of the potassium concentration remaining in solution (measured using ICP-OES). Exchangeable ions and

ECEC was performed on BRZ and CMZ while TCEC was determined for BRZ(0.1, 1 and 2M) and SCZ.

The plastic limit (w_P) and liquid limit (w_L) tests were performed using standardized equipment in accordance with ASTM D4318 (ASTM, 2010). The plasticity index (I_p) and activity (A) of the zeolite was calculated; the clay fraction (CF) is the percent of particles sized less than 2 µm. A falling head permeability test was conducted to determine the average hydraulic conductivity of the BRZ. The falling head method (ASTM, 2015) is typically used for fine-grained soils where low flow rates and permeability is anticipated (Hunt, 2005b). The sample was pre-consolidated with 98.0 kPa and saturated with deionized (DI) water, with downward permeation through the sample. The elevation head of the DI water in the burette was measured at continuous time intervals.

2.3.2 Acid Treatment

Pre-treatment of natural zeolite with acid was employed to try to optimize the adsorption capacity for Bear River and Canadian Mining zeolites. Surface acid modification was performed using sulfuric acid (H_2SO_4, Fisher Scientific Canada, purity 95 to 97% w/w) at concentrations of 0.1, 1 and 2 M. Direct acid treatment was performed, introducing H_2SO_4 to powdered zeolite with a ratio of 100 mL acid solution per gram of zeolite, agitated (200 rpm) for 30 minutes at room temperature. The H_2SO_4 solution and zeolite mixture was centrifuged and the acid treated zeolite washed repeatedly using deionized water until a near neutral pH was measured in the wash solution. The measured pH of the wash solution ranged from 6.7 to 7.4 for all direct acid treatment applications performed in this study. The acid treated zeolite was oven-dried overnight at 105°C and manually disaggregated once dry to a similar consistency as original powdered zeolite. Batch adsorptions were carried out at 0.17 m/V ratio using the previously mentioned technique.

Scanning Transmission X-ray Microscopy (STXM) produced visual verification of sodium uptake by natural (BRZ) and acid activated Bear River (BRZ(1M)) zeolite adsorbents. This synchrotron-based test was completed by deriving image difference maps. The maps depict the difference of the on- and off- resonance images and were collected at a spatial resolution of 50 nanometers (nm).

2.3.3 Adsorption Experiments

Adsorption experiments were performed in triplicate using a batch equilibrium technique. A graphical representation of the sodium sorption experiments is presented in Figure 2.1. A 5.0g zeolite sample was mixed with synthetic sodium solutions with solid to liquid (m/v) ratios of 0.17 (30mL Na^+), 0.25 (20mL Na^+) and 0.50 (10mL Na^+). The m/V ratios were chosen for this study based on previous findings for zeolite ion exchange (Inglezakis, 2005; Ganjegunte et al., 2011; Belbase et al., 2013). The sodium concentrations in the synthetic solutions ranged from 250 to 10,000 mg/L Na^+ (10.9 to 435 meq/L). The mixture was agitated at 200 rpm using a reciprocal shaker (New Brunswick Scientific Co. Laboratory Rotator – G2) for 24-hours at room temperature (approx. 23°C). A centrifuge (Eppendorf 5804R-15 amp) was used to separate the suspension with the effluent kept for Na^+ concentration analysis using a sodium selective electrode (Thermoscientific ROSS Sodium Ion Selective Electrode and Orion Star A214 Benchtop Meter). The sodium selective electrode and ICP-OES outputs cation concentrations in a solution in milligrams per litre (mg/L). With the exception of the sorption isotherms, the data in this study presented the concentration of ions adsorbed using milliequivalents per litre (meq/L). The equivalent weight of an ion is the molecular weight divided by the valence charge. The equivalent weight was used to convert the ion concentrations from mg/L to meq/L for data analysis. The pH of the sorption solutions were measured upon completion of each batch adsorption experiment using a Hach HQ40d multi meter (PHC28101).

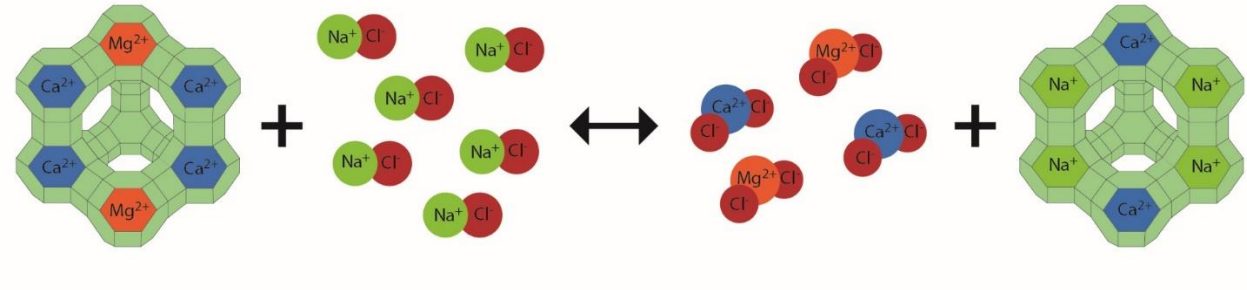


Figure 2.1: Graphical representation of natural zeolite undergoing ion exchange with sodium chloride.

Batch adsorption experiments were conducted using natural clinoptilolite-rich adsorbents, BRZ, CMZ and SCZ, as well as acid treated zeolites. The acid treatment and sodium sorption processes are presented in Figure 2.2.

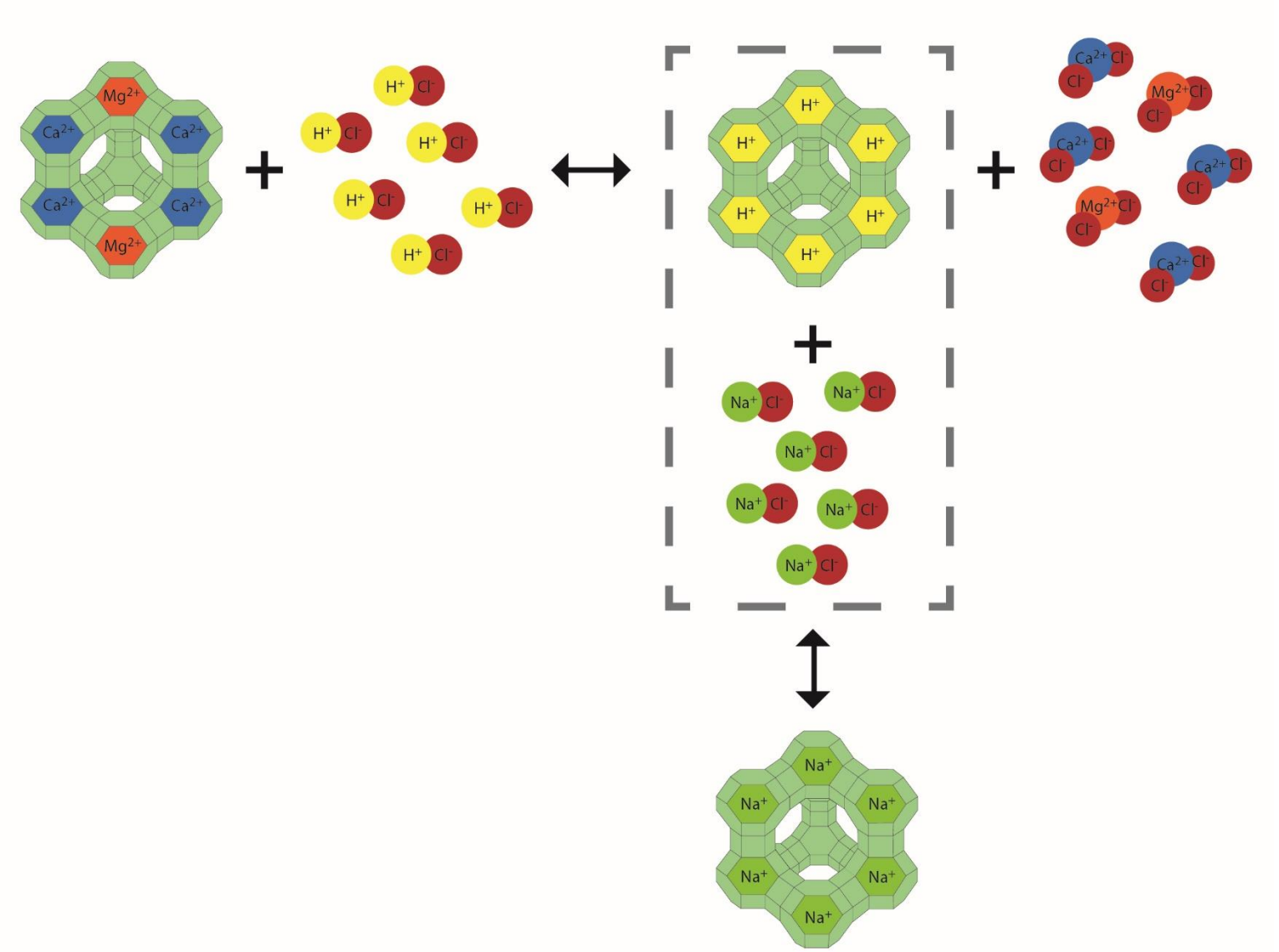


Figure 2.2: Graphical representation of acid modification of natural zeolite followed by sodium sorption with the protonic zeolite form.

2.3.3.1 Sodium Desorption

Deionized (DI) water was used as a sorbate solution in conjunction with the batch adsorption experiments conducted on natural and acid treated BRZ's. This technique allowed the concentration of sodium ions desorbing from the sodium-zeolite to be evaluated. Batch adsorption experiments were first conducted using a range of Na^+ concentrations (250, 500, 750 and 1,000 mg/L) and re-using the Na^+-zeolite adsorbent for sorption with DI water. The sorption experiment was completed using the previously described batch adsorption techniques including analyzing the sorption solution for sodium concentration using the ion selective electrode.

2.3.3.2 Simulated Potash Brine Impacted Groundwater

Potash brine impacted water was simulated with groundwater spiked with varying potash brine volumes to create designated sodium concentrations ranging from 500 to 10,000 mg/L Na^+ (21.7 to 435 meq/L). The brine spiked groundwater (PB + GW) was added to zeolite for batch adsorption experiments at a m/V ratio of 0.17. The mixture was agitated at 200 rpm for 24 hours at room temperature. The zeolite-PB + GW mixture was separated using a centrifuge with the effluent kept refrigerated at 4°C until analyzed. Sodium removal by BRZ, BRZ(1M) and CMZ was evaluated using the sodium selective electrode throughout the initial concentration range. Ion concentrations for Na^+, Ca^{2+}, Mg^{2+} and K^+ were analyzed by ICP-OES to determine zeolite selectivity sequences from CEC experiments and batch adsorption experiments using initial PB + GW sodium concentration of 500 mg/L (21.8 meq/L).

2.3.4 Statistical Analysis

Adsorption experiments were conducted in triplicate throughout the study. Verification of the experimental data was performed using GraphPad Prism (Version 6) and statistical analysis techniques including the t-test as well as one- and two-way ANOVA. The statistical significance was determined using multiple comparison calculations using Bonferroni method, other than for comparisons with a control value which used Dunnett. The multiple comparison analysis was calculated with a significance level (p-value) of 0.05 (95% confidence interval); the significance levels within the figures are summarized as: $p \leq 0.05$ (*), $p \leq 0.01$ (**), $p \leq 0.001$ (***), and $p \leq 0.0001$ (****) with no asterisk meaning the hypothesis is not statistically significant ($p > 0.05$).

2.4 Results

2.4.1 Material Characterization

A cation chemistry analysis was performed on samples of groundwater, potash brine and potash brine spiked groundwater at approximately 500 mg/L Na^+ (PB+GW(500)) using ICP-OES; this data is summarized in Table 2.1 with the complete data set shown in the supplementary data (Table 2.8). The SAR of the groundwater, potash brine and PB + GW (500) was 0.26, 350 and 12.1 respectively. The three samples were all determined to be very hard, with total hardness values above 180 mg/L as $CaCO_3$ (Canada, 1979).

Table 2.1: Water chemistry of potash tailings brine, groundwater and brine spiked groundwater (PB + GW (500)) measured externally using ICP-OES.

		Brine	Groundwater	PB + GW (500)
Ion Concentration (mg/L)	Na^+	89,500	12	469
	Ca^{2+}	2,000	111	49
	Mg^{2+}	1,800	32	40
	K^+	58,200	3.0	258
	Cl^-	219,000	14	1060
	SO_4^{2-}	1,800	30	39
	HCO_3^-	73	461	443
	pH	7.22	8.34	7.95
T. Hardness (mg/L as $CaCO_3$)		12,380	409	457
SAR		350	0.26	12.1

[1] – Total Hardness (mg/L as $CaCO_3$) = $2.5[Ca^{2+}] + 4.1[Mg^{2+}]$

Previous adsorption studies have reported an increase in the maximum adsorption capacity and larger SAR reduction with smallerzeolite particle sizes (Pansini, 1996; Belbase et al., 2013; Vivacqua et al., 2013). It was important to pulverize the zeolite to obtain sample uniformity as well as try to optimize adsorption efficiency. Smaller particles create a larger surface area and shorter diffusion pathways within the framework channels (Cui et al., 2006). The particle size distribution curve in Figure 2.3 shows similar gradation among zeolite samples, with the exception of a higher percentage of finer particle sizes for CMZ.

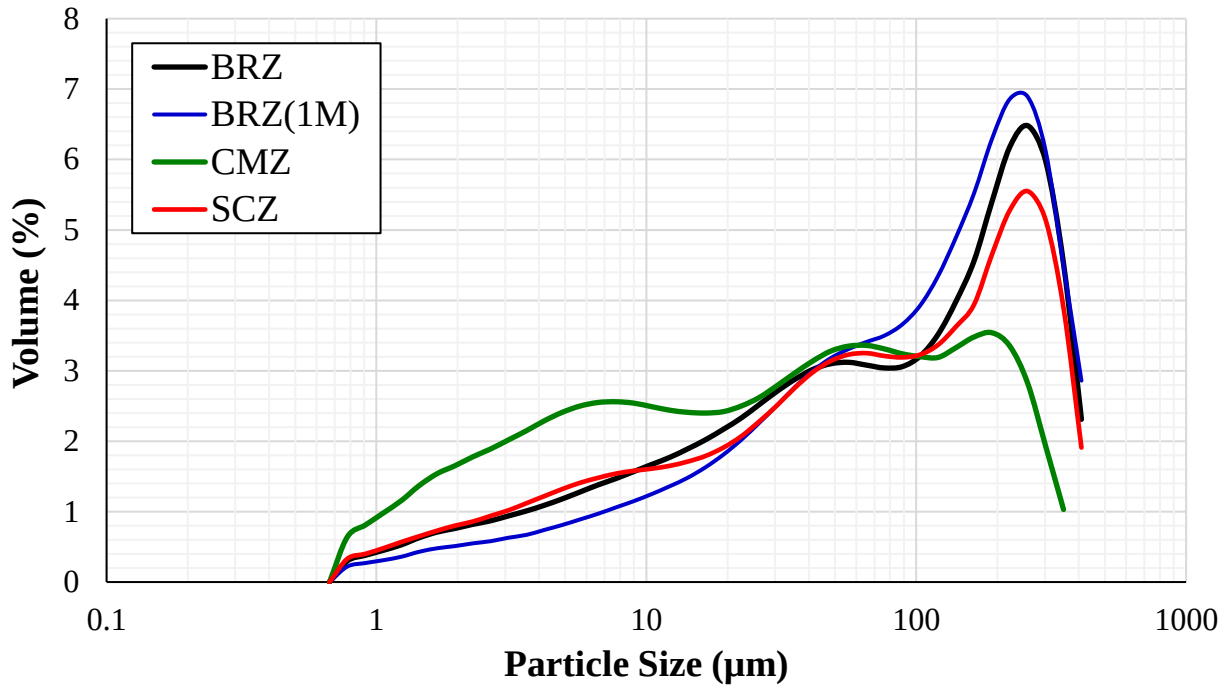


Figure 2.3: Particle size distribution graph for BRZ, BRZ(1M), CMZ and SCZ.

X-ray techniques were useful for characterizing the zeolites mineralogical and chemical compositions. The x-ray diffraction analysis of BRZ, BRZ(1M), and CMZ provided clinoptilolite compositions of 85.6%, 86.1%, and 69.3% respectively. XRD analysis determined the remainder is comprised of illite, quartz and cristobalite (see Table 2.9 in the supplementary data for numerical analytical results); these silicate class minerals are often referred to as impurities (Curkovic et al., 1996; Inglezakis et al., 2001). Illite should have minimal negative effect on the exchange capacity due to its relatively high CEC, while quartz and cristobalite lack aluminum atoms and the associated negative charge, making them inactive for ion exchange (Inglezakis, 2005). X-ray fluorescence (XRF) analyses outlined the chemical compositions of BRZ, BRZ(1M) and CMZ, shown in Table 2.2. Using the weights of SiO_2 and Al_2O_3, the Si/Al ratios were estimated to be 6.2, 6.8 and 5.5 for BRZ, BRZ(1M), and CMZ respectively. Clinoptilolite has the highest Si/Al ratios of the natural zeolites (Breck, 1984) with a range of 4.0 to 5.5 (Erdem et al., 2004; Santiago et al., 2016). The slightly increased Si/Al ratio for BRZ(1M) suggests that Al^{3+} was released from the framework as a result of acid treatment (Haldun Kurama et al., 2002; Cheng et al., 2005), with the minimal change likely due to incomplete protonation.

Table 2.2: XRF chemical composition of the BRZ, CMZ, SCZ and BRZ(1M) in weight percent for major oxides.

Zeolite	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Si/Al
BRZ	64.92	8.83	1.90	0.49	2.74	<0.01	3.75	0.28	0.03	0.05	6.2
CMZ	72.85	11.32	2.29	0.38	1.32	3.17	3.02	0.14	0.00	0.02	5.5
SCZ [1]	70.0	12.1	1.6	1.5	3.4	0.3	3.0	—	—	0.05	4.9
BRZ(1M)	74.33	9.27	2.12	0.51	1.95	<0.01	2.93	0.32	0.04	0.06	6.8

[1] – SCZ chemical analysis obtained from manufacturer specifications (St. Cloud Mining Company, 2013).

The cation exchange capacity, primary exchangeable ions and BET surface area are listed in Table 2.3. The exchangeable cations were released during NH_4^+ exchange and follow an abundance sequence of $Ca^{2+}>K^+>Na^+>Mg^{2+}$ for BRZ and $K^+>Na^+>Ca^{2+}>Mg^{2+}$ for CMZ. The summation of the exchangeable cations yielded an effective CEC of 138.4 and 100.5 meq/100g for BRZ and CMZ respectively. The 1.0M H_2SO_4 BRZM yielded the highest TCEC at 158.7 meq/100g followed by BRZ(0.1M) and BRZ(2M) with 123.4 and 118.3 meq/100g respectively. Analysis of CEC's for multiple clinoptilolite samples, obtained worldwide, suggests a CEC within the range of 60 to 180 meq/100g (Wang and Peng, 2010). Table 2.3 also outlines the BET-N_2 surface area results. The natural zeolite samples had similar surface areas of 37 and 32 m^2/g for BRZ and CMZ respectively. When comparing the natural and acid treated surface areas for the Bear River samples, the BET surface area gradually increased for the 0.1M and 1.0M H_2SO_4 acid treatments over BRZ. The structure potentially began to collapse at higher acid concentrations (2M H_2SO_4), suggesting a smaller surface area increase; BRZ(1M) had a BET surface area of 66 m^2/g compared to 69 m^2/g for BRZ(2M).

Table 2.3: Cation exchange capacity and BET surface area for natural and acid treated zeolites. Values represent the mean results and standard deviation.

Zeolite	Exchangeable Ions (meq/100g)				CEC (meq/100g)	BET – N_2 (m^2/g)
	Na^+	Ca^{2+}	Mg^{2+}	K^+		
BRZ	18.6 ± 0.1	66.5 ± 0.1	3.4 ± 0.1	41.6 ± 1.2	138.4 ± 5.5 [1]	37
CMZ	33.2 ± 0.5	29.5 ± 1.1	1.8 ± 0.1	39.2 ± 0.4	100.5 ± 4.6 [1]	32
SCZ	—	—	—	—	127.0 ± 10.6 [2]	—
BRZ(0.1M)	—	—	—	—	123.4 ± 5.6 [2]	47
BRZ(1M)	—	—	—	—	158.7 ± 6.8 [2]	66
BRZ(2M)	—	—	—	—	118.3 ± 1.6 [2]	69

[1] – Effective cation exchange capacity (ECEC)
[2] – Total cation exchange capacity (TCEC)

Particle size distribution, consistency limits, index properties and hydraulic conductivity are useful engineering properties for suggesting future applications. Based on adsorption performance, the engineering properties were measured for the Bear River zeolite sample. The liquid and plastic limits of the BRZ are 45.62% and 40.20 % respectively, yielding a plasticity index ($I_p = w_L - w_p$) of 5.42. An activity of 1.44 was calculated, suggesting a chemically reactive clay (Hunt, 2005b). A falling head permeability test was conducted with 98 kPa stress on the saturated zeolite; BRZ's average hydraulic conductivity was 4.32×10^{-8} m/s. Previous studies have measured the hydraulic conductivity of Turkish zeolites with results ranging from 10^{-5} to 10^{-9} m/s (Oren and Ozdamar, 2013). The hydraulic conductivity will vary with the degree of compaction, zeolite mineral content and particle size distribution (Kayabali, 1997).

2.4.2 Sodium sorption using synthetic solutions

2.4.2.1 Natural zeolite adsorbents

Adsorption isotherms describe the retention of the ion from an aqueous solution to a solid phase media. The mass of Na^+ adsorbed on the zeolite, q (mg/g) was calculated using Equation 2.2 where C_e is the Na^+ concentration remaining in the effluent solution (mg/L), C_0 is the initial Na^+ concentration, V is the volume of concentrated Na^+ solution used (L) and m is the mass of zeolite adsorbent (g) (Ghaly and Verma, 2008):

$$q = \frac{V \times (C_e - C_0)}{m} \tag{2.2}$$

Langmuir and Freundlich isotherm models generated Na^+ adsorption isotherms for natural clinoptilolie-rich zeolites at three mass of zeolite to volume of Na^+ solution (m/V) ratios of 0.17, 0.25 and 0.50. The Langmuir model can be described as (Volesky, 2003; Foo and Hameed, 2010):

$$q = \frac{q_e K_L C_e}{1 + K_L C_e} \tag{2.3}$$

where q_e is the maximum adsorption capacity of the zeolite (mg/g), K_L is the Langmuir coefficient related to the affinity between the sodium and zeolite (Volesky, 2003). The Langmuir model was developed based on the concept that adsorption can only occur at a finite number of adsorption sites (Fetter, 1993), equal energy among adsorption sites (Xue et al., 2014) and assumes monolayer adsorption (Bibiano-Cruz et al., 2016). The Freundlich model assumes multilayer adsorption on heterogeneous adsorption sites and can be described as (Fetter, 1993):

$$q = K_F C_e^{1/n} \tag{2.4}$$

where K_F [(mg/g)(L/mg)$^{1/n}$] is the Freundlich constant and n is the dimensionless Freundlich exponent. The Langmuir and Freundlich models were applied to the experimental data based on the non-linear squares method; Araike's Information Criterion (AIC) was used to assess the fit of the models (El-Khaiary and Malash, 2011).

$$AIC = N ln \frac{SSE}{N} + 2N_P + \frac{2N_P(N_P + 1)}{N - N_P - 1} \tag{2.5}$$

where N refers to the number of data points, SSE is the sum of squared deviations of the points from the regression curve and N_P is the number or parameters in the associated models. The evidence ratio was used to compare the AIC values of the two models and is computed using the following formula, where ΔAIC is the absolute value of the difference in AIC values for the Langmuir and Freundlich models:

$$Evidence\ Ratio = e^{0.5(\Delta AIC)} \tag{2.6}$$

Sodium sorption Langmuir isotherms for natural clinoptilolie-rich zeolites (BRZ, CMZ and SCZ) were generated at three mass of zeolite to volume of Na^+ solution (m/V) ratios of 0.17, 0.25 and 0.50, as shown in Figure 2.4, Figure 2.13 and Figure 2.14 respectively. Figures 2.13 and 2.14 are included in Section 2.7.2 of the supplementary data.

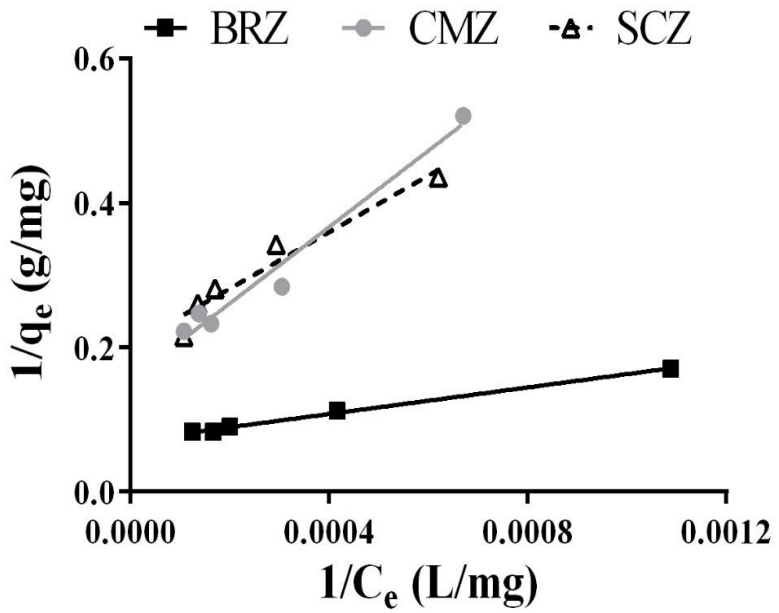


Figure 2.4: Langmuir isotherm analysis for natural zeolites, BRZ, SMZ and CMZ at a mass to volume ratio of 0.17. The mean pH values for the initial Na^+ concentration range was 6.26±0.18 and the pH of the BRZ, CMZ and SCZ sorption solutions were 7.01 ± 0.09, 5.84 ± 0.04 and 7.23 ± 0.08 respectively.

The Langmuir and Freundlich isotherm model parameters for Na^+ adsorption onto BRZ, CMZ and SCZ, at a mass to volume ratio of 0.17, are presented in Table 2.4. The isotherms for Na^+ uptake by BRZ and CMZ, created curves which were described well by the Langmuir model. The evidence ratio for BRZ, suggests that the Langmuir model is approximately 36 times more likely to be accurate than the Freundlich model. The maximum adsorption capacities were determined from the Langmuir equation to be 14.3 ± 0.4 and 5.8 ± 0.5 mg/g for BRZ and CMZ respectively. The Freundlich model provided a good fit for SCZ, with an evidence ratio of 12.3. The isotherms and model parameters for Na^+ sorption onto BRZ, CMZ and SCZ at mass to volume ratios of 0.25 and 0.5, are presented in the supplementary data (Figure 2.13 and Table 2.10, and Figure 2.14 and Table 2.11 respectively). At this stage in the study, SCZ was eliminated as an adsorbent due to the consistent increased Na^+ uptake behavior by BRZ and the localized proximity of CMZ.

Table 2.4: Isotherm model parameters from the non-linear squares analysis for batch adsorption experiments conducted on BRZ, CMZ and SCZ at a mass to volume ratio of 0.17.

Model	Parameters	*BRZ*	CMZ	SCZ
Langmuir	q_e (mg/g)	14.3 ± 0.4	5.8 ± 0.5	5.6 ± 0.7
	K_L	0.0007 ± 0.00008	0.0004 ± 0.00004	0.0004 ± 0.00001
	R^2	0.992	0.950	0.905
	Sy.x	0.28	0.27	0.32
Freundlich	K_F [(mg/g)(L/mg)$^{1/n}$]	0.71 ± 0.25	0.14 ± 0.11	0.11 ± 0.05
	n	3.1 ± 0.4	2.6 ± 0.6	2.5 ± 0.3
	R^2	0.964	0.891	0.965
	Sy.x	0.58	0.40	0.19
Δ AIC		-7.25	-3.91	5.02
Evidence Ratio		37.5	7.1	12.3
Preferred Model		Langmuir	Langmuir	Freundlich

± – corresponds to the standard error

BRZ was used to evaluate the mass of zeolite to volume of Na^+ ratios of 0.17, 0.25 and 0.50. The nonlinear squares method was applied to evaluate Langmuir and Freundlich isotherm models; the results are summarized in Table 2.5, with the model parameters supplied in Table 2.4 for a m/V ratio of 0.17 and in the supplementary data (Table 2.10 for 0.25 and Table 2.11 for 0.5). The 0.17 m/V ratio, produced a slightly higher average maximum adsorption capacity of 14.3 ± 0.4 mg/g compared to 13.8 ± 0.6 and 13.3 ± 0.4 mg/g for 0.25 and 0.50 m/V respectively. Evaluating multiple ratios indicated a higher volume of sodium solution could be treated with a consistent mass of zeolite. The average pH response measured amongst the m/V ratio sorption solutions was 7.0 ± 0.1.

Table 2.5: Parameters from the nonlinear squares analysis for Na^+ removal by BRZ at varying mass zeolite to volume Na^+ solution (m/V) ratios. Values represent the mean and standard deviation.

m/V Ratio	q_e (mg Na^+/g zeolite)	R^2	Preferred Model	Evidence Ratio
0.17	14.3 ± 0.4	0.992	Langmuir	37.5
0.25	13.8 ± 0.6	0.991	Freundlich	1.0
0.50	13.3 ± 0.4	0.998	Langmuir	223

2.4.2.2 Acid Treated Zeolite Adsorbents

The influence on sodium removal by acid activated zeolite adsorbents was investigated. Sodium sorption is shown in Figure 2.5(A) for the 0.1, 1.0, and 2M H_2SO_4 treated zeolites. The concentration of sodium remaining after sorption with the acid treated zeolites, does not follow a consistent trend for the initial Na^+ concentration range. At 10.9 meq/L (250 mg/L) Na^+, the concentration of sodium remaining after sorption, decreases as the acid concentration increases; however, the difference in the uptake of Na^+ ions by BRZ(1M) and BRZ(2M) is insignificant ($p>0.05$) from 21.8 to 43.5 meq/L (500 to 1,000 mg/L). The 1M H_2SO_4 treated BRZ was significantly more efficient ($p \leq 0.0001$) for sodium removal at 87.0 meq/L (2,000 mg/L). BRZ(1M) is suggested as the optimum activated zeolite in this study due to its consistency and behavior at higher sodium concentrations. Figure 2.5(B) shows the average pH response for BRZ(0.1M), BRZ(1M) and BRZ(2M). The pH of the acid treated solutions decreased significantly during adsorption ($p \leq 0.0001$) with the pH decreasing as the sodium concentration increased.

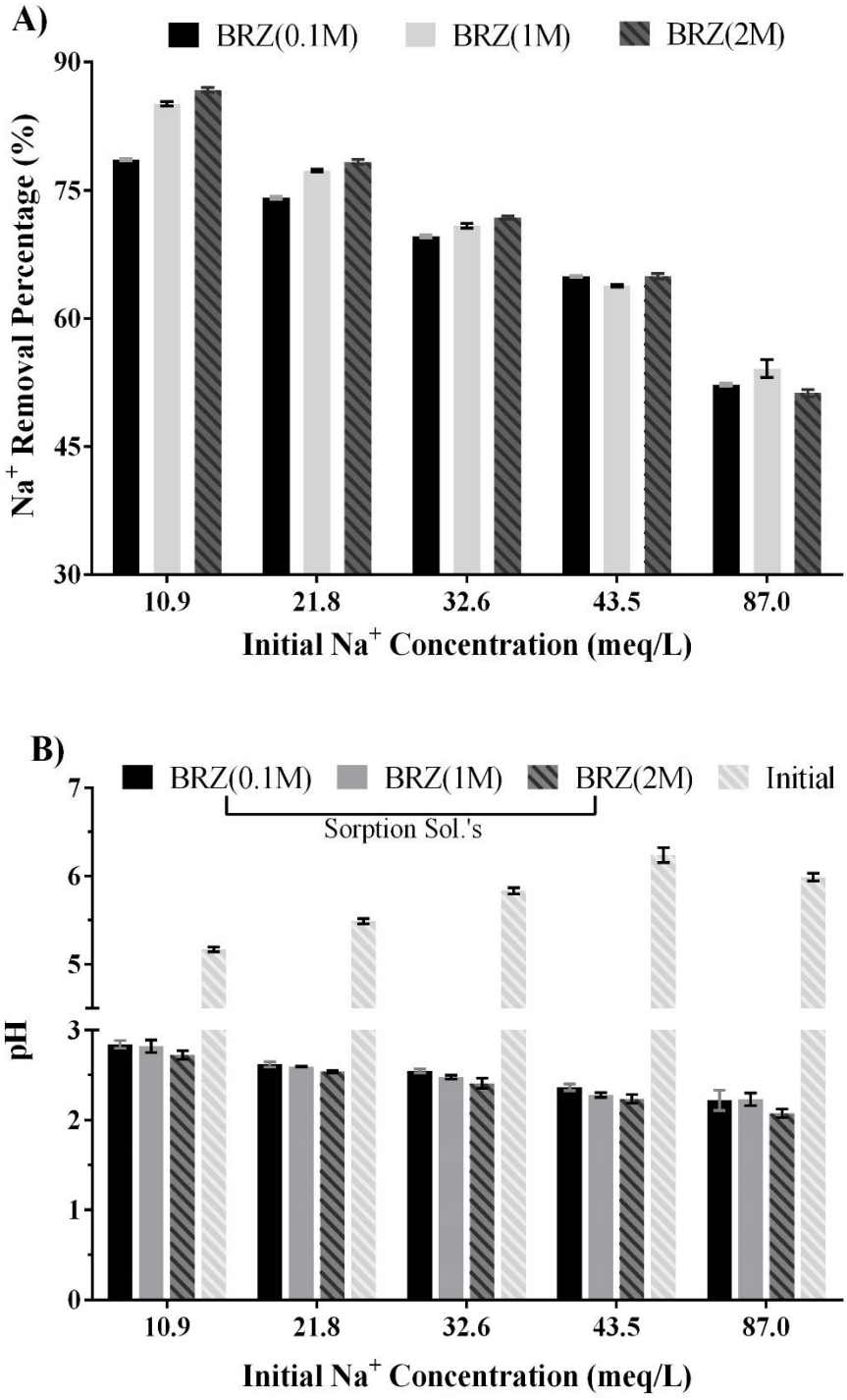


Figure 2.5: (A) Sodium sorption as a function of acid treated BR zeolites with sulfuric acid concentrations of 0.1, 1 and 2M and (B) the resulting mean pH values of the sorption and initial solutions. The batch adsorption experiments were conducted using synthetic sodium solutions at an m/V ratio of 0.17 and values represent the mean results and standard deviation.

Figure 2.6 evaluated sodium uptake and pH response of natural and acid activated Bear River and zeolite adsorbents. The sodium sorption uptake is shown in Figure 2.6(A) for natural (BRZ) and acid treated (BRZ(1M)) adsorbents over an Na^+ range of 10.9 to 435 meq/L (250 to10,000 mg/L). The BRZ and BRZ(1M) curves converge as the Na^+ concentration increases, the difference becoming insignificant at 43.5 meq/L Na^+ ($p>0.05$). At 10.9 meq/L Na^+, BRZ(1M) removed approximately 17% more sodium than its natural counterpart ($p \leq 0.0001$); this variance at 87.0 meq/L Na^+ was less than 3% ($p>0.05$). In Figure 2.6(B), the pH response of the BRZ(1M) sorption solutions decreased as initial Na^+ concentrations increased; the average pH at 10.9 and 435 meq/L Na^+ is 2.87 ± 0.03 and 1.92 ± 0.04 respectively. As more Na^+ cations are exchanged, the hydrogen ions present on the acid treated zeolite exchange sites are released into solution, accounting for the successive decrease in pH. While ion exchange using the natural zeolite kept the pH near neutral (average of 7.05 ± 0.03 for BRZ), the treated zeolites created acidic conditions in the sorption solution which is problematic for practical applications. The Canadian Mining zeolite also underwent acid pretreatment with 1M H_2SO_4; preliminary Na^+ sorption results are presented in Figure 2.15 in the supplementary data. Acid modification increased the Na^+ uptake; however, the performance of CMZ(1M) was consistently low, removing approximately 15% less Na^+ than BRZ(1M) at 87 meq/L as shown in Figure 2.16. CMZ(1M) was eliminated from future modification experiments at this time.

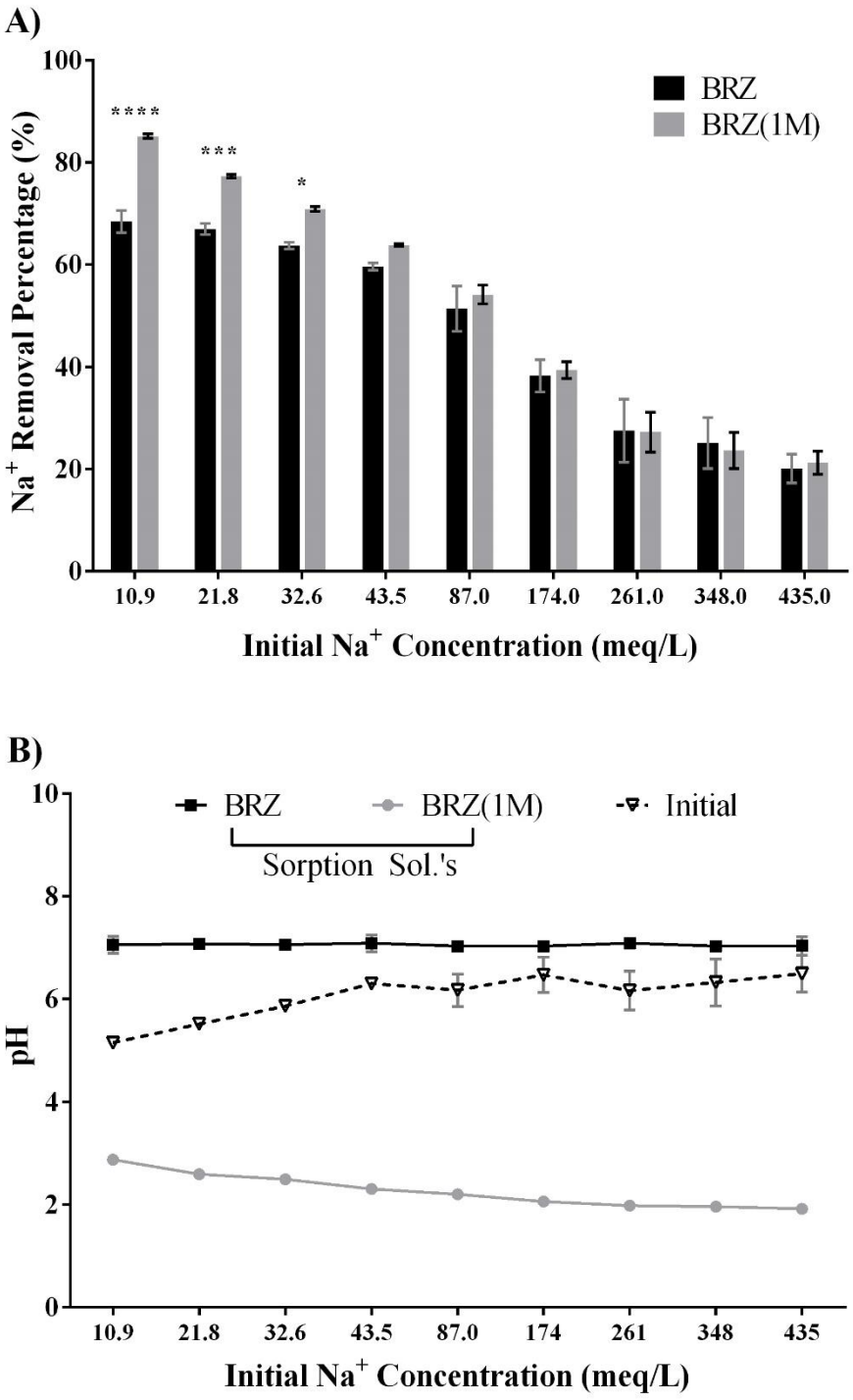
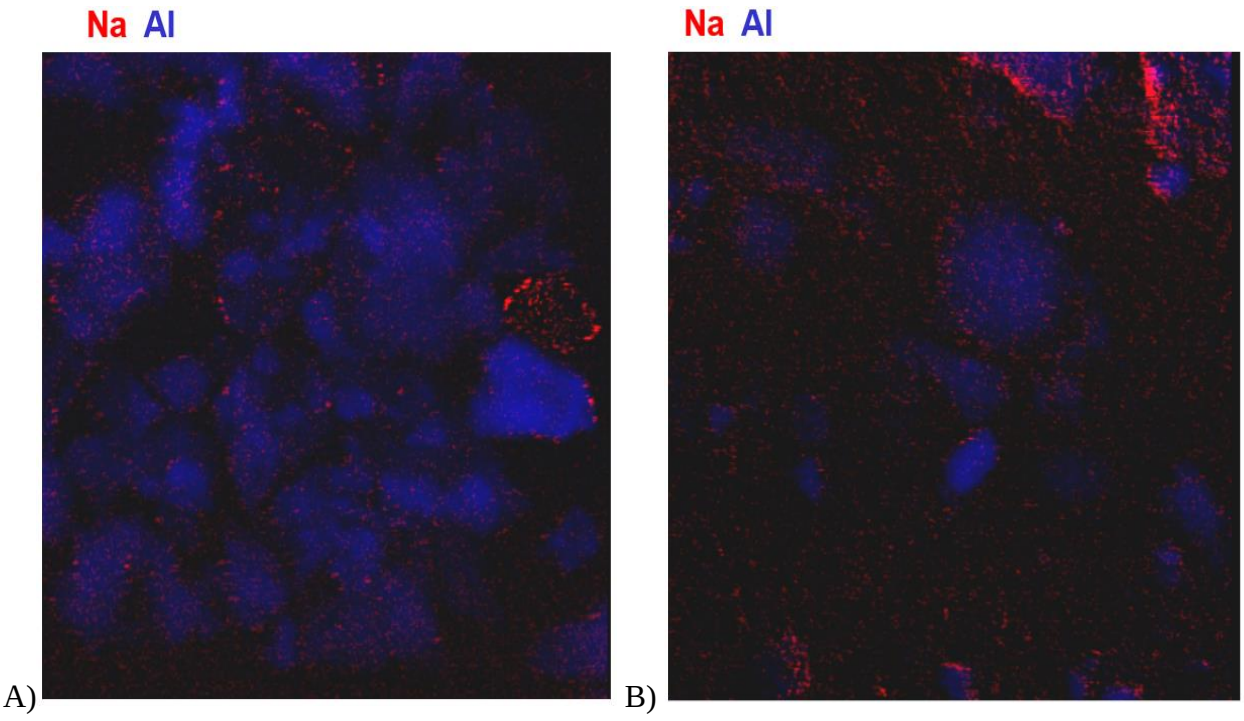


Figure 2.6: Evaluating the effect of acid treatment (using 1M H_2SO_4) on sodium uptake for (A) Bear River adsorbents at an m/V ratio of 0.17. The average pH responses of the adsorption effluents in comparison to the initial sodium solution pH for BR zeolites (B). Values represent the mean results and standard deviation.

The synchrotron-based STXM elemental maps are shown in Figure 2.7 with an initial synthetic Na^+ concentration of 21.75 meq/L and BRZ (A) and BRZ(1M) (B) adsorbents. Visual verification of the enhanced sodium uptake by BRZ(1M) over BRZ can be seen by comparing the red/pink color markings in both images. The corresponding adsorbed concentrations for BRZ and BRZ(1M) are 14.7 ± 0.2 and 17.0 ± 0.1 meq/L Na^+ respectively. Evaluation of aluminum, shown in blue, for natural (A) and 1M H_2SO_4 treated (B) Bear River zeolites, suggest dealumination occurred as a result of acid activation.



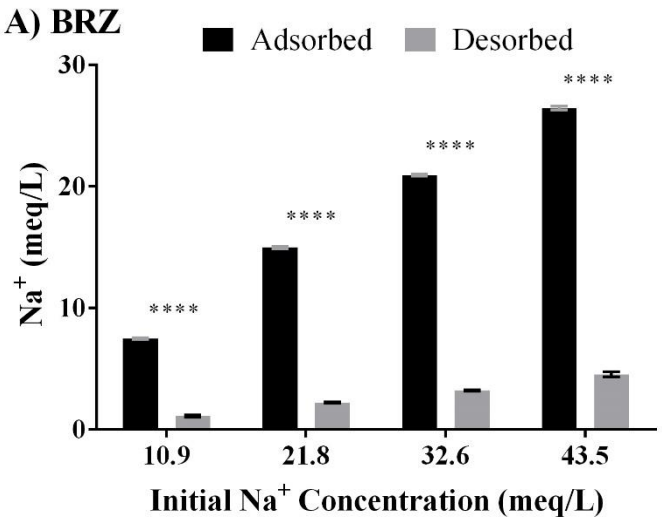
A) B)

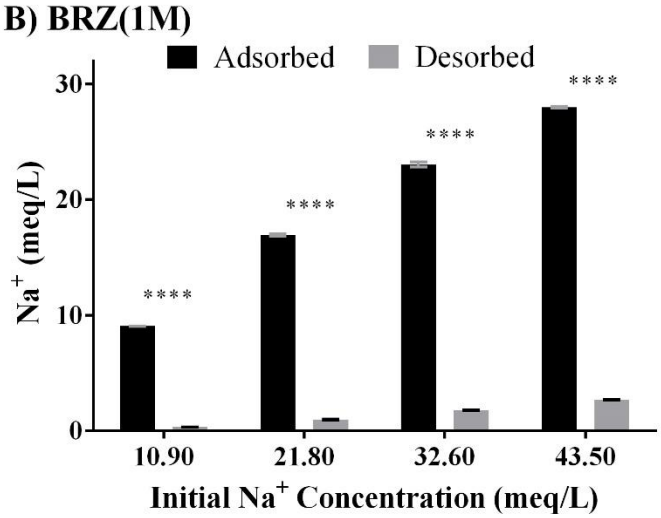
Figure 2.7: STXM elemental maps with sodium in red and aluminum in blue for (A) BRZ and (B) BRZ(1M). A batch adsorption experiment was performed prior to the synchrotron-based analysis with an initial Na^+ concentration of 21.8 meq/L (500 mg/L from NaCl), pH of 5.51 ± 0.04 and m/V ratio of 0.17. The pH of the effluent solutions for BRZ and BRZ(1M) were 7.07 ± 0.04 and 2.59 ± 0.05 respectively.

2.4.2.3 Sodium Desorption

Desorption of sodium ions from Na^+-zeolite was investigated with DI water and Na^+-zeolite batch adsorption experiments. The Na^+ desorbed was calculated as the difference between Na^+ adsorbed during sodium adsorption experiment and the Na^+ measured from the DI sorption solution. The adsorption and desorption of sodium ions is shown in Figure 2.8 for BRZ (A) and BRZ(1M) (B). The difference between adsorption and desorption is significant ($p \leq 0.0001$) for both adsorbents

at initial Na^+ concentrations of 10.9 to 43.5 meq/L. An initial Na^+ concentration of 21.8 meq/L, suggested 14.8 ± 0.2 % and 5.8 ± 0.2 % desorption of Na^+ from the sodium forms of BRZ and BRZ(1M) respectively. A graphical representation of the comparison of Na^+ desorption for BRZ and BRZ(1M) is presented in Figure 2.17 in the supplementary material, suggesting the difference is statistically significant. The natural zeolite desorbed significantly more sodium than the acid treated zeolite throughout the initial Na^+ solution range ($p \leq 0.0001$); this phenomenon has been suggested previously for Cu^{2+} ions (Panayotova, 2001). The pH of the BRZ sorption solution increases after exposure to Na^+ solution and decreases when mixed with DI water; the inverse was found for BRZ(1M)'s pH response (Figure 2.8(C)).





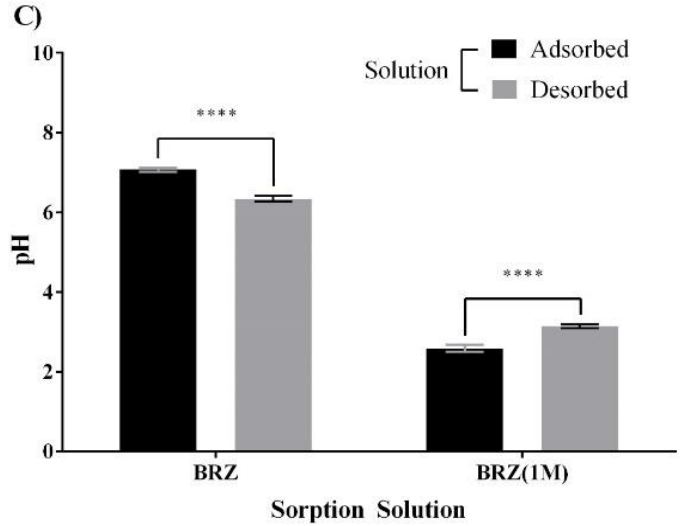
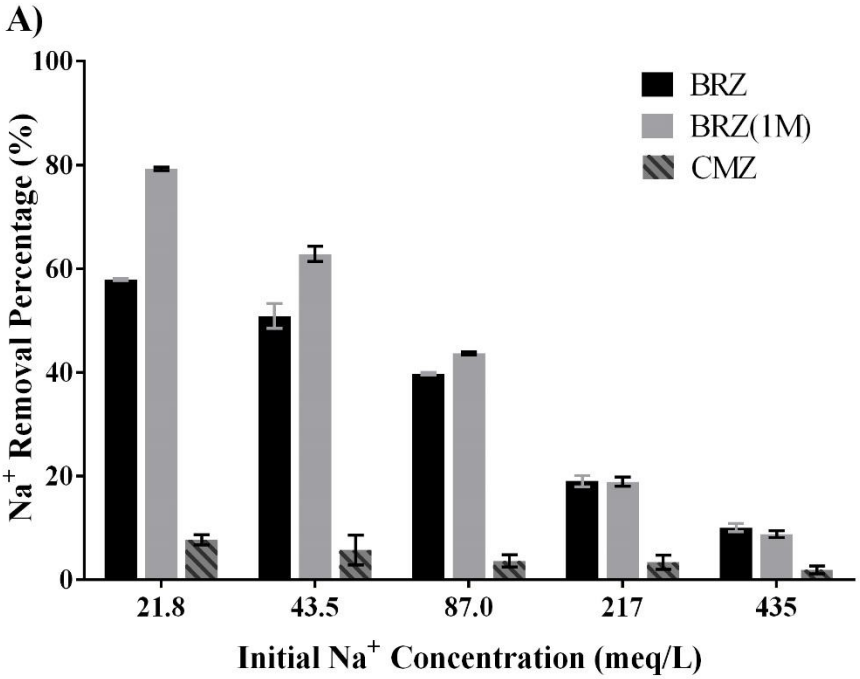


Figure 2.8: Batch adsorption and desorption data for (A) BRZ and (B) BRZ(1M). Values represent the mean results and standard deviation. The pH from the adsorption and desorption solutions (C) was measured using an initial concentration of 21.8 meq/L (500 mg/L) Na^+ (pH = 5.51 ± 0.04) and DI water (pH = 4.99 ± 0.74).

2.4.3 Potash Brine Spiked Groundwater Sorption Experiments

The sodium removal potential of BRZ, BRZ(1M) and CMZ was simulated with potash brine spiked groundwater (V/V) at 21.8, 43.5, 87.0, 218 and 435 meq/L Na^+. Figure 2.9(A) shows the BRZ(1M) removing more Na^+ at lower initial concentrations before converging towards BRZ, for an insignificant difference at concentrations above 218 meq/L Na^+ ($p>0.05$). Both BRZ and BRZ(1M) removed significantly ($p\leq0.0001$) more Na^+ than CMZ throughout the initial PB+GW Na^+ concentration range; Na^+ uptake at 21.75 meq/L initially was observed to be 7.7 ± 0.8 % for CMZ compared to 57.9 ± 0.2 % for BRZ and 79.3 ± 0.3 % for 1M H_2SO_4 treated Bear River zeolite. Adsorption isotherms for Na^+ adsorption from PB+GW is presented in the supplementary data (Figure 2.18 and Table 2.13). The Langmuir model described the data well for BRZ, BRZ(1M) and CMZ, with maximum adsorption capacities calculated to be 6.5 ± 0.2, 5.7 ± 0.2 and 1.7 ± 0.3 mg/g respectively. The low Na^+ adsorption by CMZ resulted in its removal from future PB+GW experiments in this study. The pH of the initial and sorption solutions is shown in Figure 2.9(B). The pH values of the initial PB+GW solutions vary significantly to the three sorption solutions for each initial sodium concentration ($p\leq0.0001$). The BRZ(1M) produced a statistically significant ($p\leq0.0001$) pH response compared to the sorption solutions for BRZ and CMZ; however, the difference in pH between the natural zeolites was insignificant ($p>0.05$).



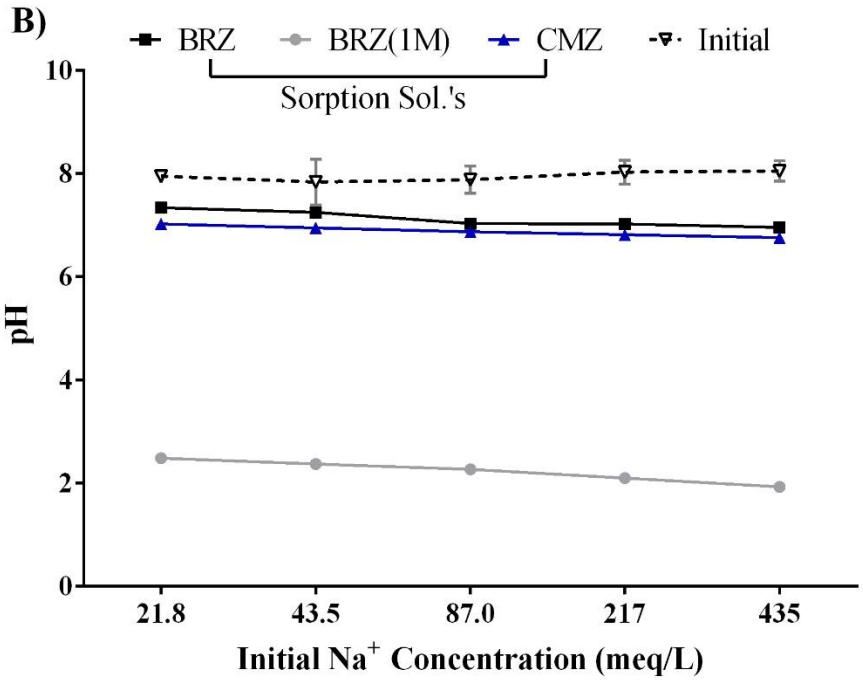


Figure 2.9: The result of adsorption experiments for PB+GW over a sodium concentration range of 500-10,000 mg/L and m/V ratio of 0.17. The sodium uptake (A) and effluent pH (B) were analyzed for BRZ, BRZ(1M) and CMZ. Values represent the mean results and standard deviation.

2.4.3.1 Effect of Competing Ions

The influence other ions present in the PB+GW had on sodium uptake was investigated over an initial Na^+ concentration range of 21.8 to 435 meq/L. Figure 2.10 contains the sodium concentrations of BRZ (A) and BRZ(1M) (B) sorption solutions from synthetic Na^+ solutions and PB + GW. Both sorbents were able to adsorb more Na^+ from synthetic solutions than PB+GW; BRZ and BRZ(1M) removed approximately 10% ($p \leq 0.001$) and 3% ($p > 0.05$) more Na^+ from 21.75 meq/L Na^+ synthetic solutions. The variation in Na^+ uptake from synthetic and PB+GW solutions diverged as the Na^+ concentration increased, becoming statistically significant with $p \leq 0.0001$. As shown in Figure 2.10(C), the difference between the pH values for the synthetic and PB+GW solutions was insignificant among the sorption solutions ($p > 0.05$) while being statistically significant for the initial solutions ($p \leq 0.0001$). The pH increase associated with the slightly acidic synthetic sorption solutions, suggest some H^+ uptake occurred along with Na^+ during adsorption. The pH decrease associated with an alkaline PB+GW may be a result of an OH^- reaction with the zeolites external surface; however, these sites are still available for cation exchange (Huang and

Natrajan, 2006). As anticipated, the pH response of BRZ(1M) sorption solution, shown in Figure 2.10(D), is significantly lower than the initial pH for both the synthetic and PB+GW solutions ($p \leq 0.0001$).

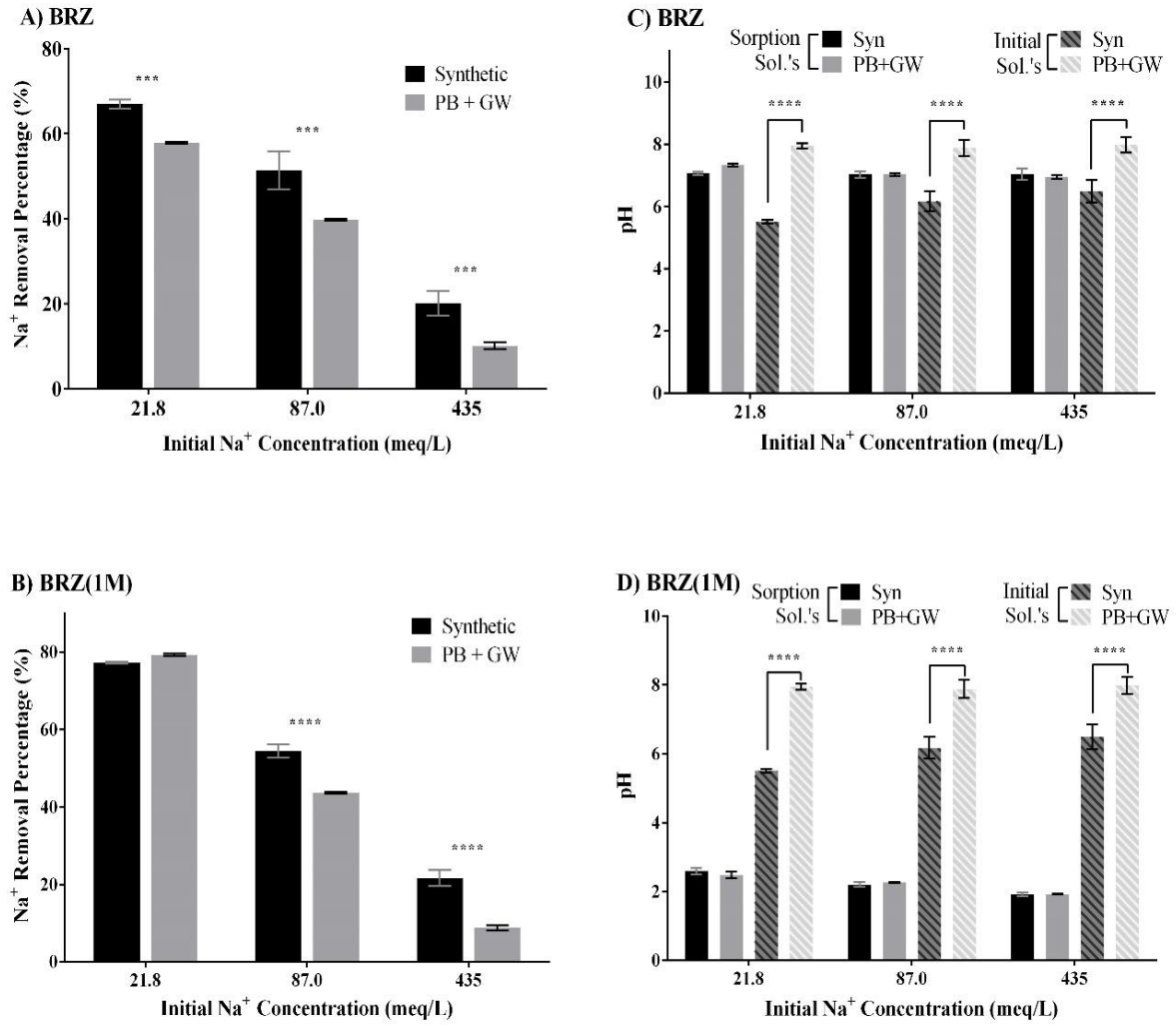
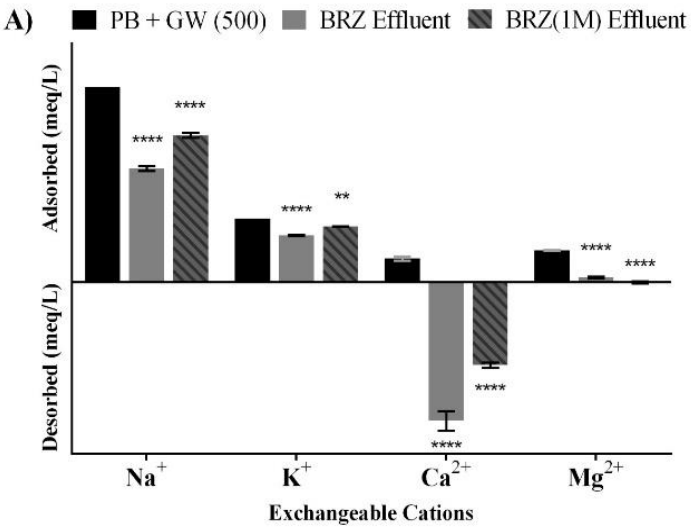


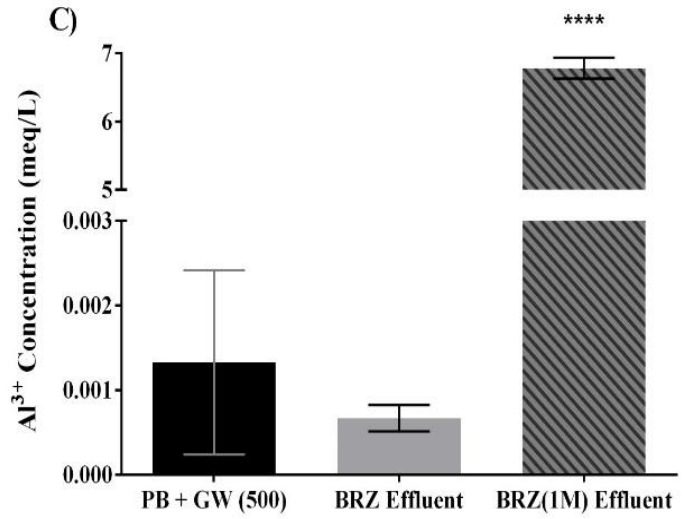
Figure 2.10: Sodium removal efficiencies for (A) BRZ and (B) BRZ(1M) adsorbents with synthetic solutions and potash brine spiked groundwater (PB + GW). Values represent the mean results and standard deviation. The mean pH responses of the sorption solution for (C) BRZ and (D) BRZ(1M).

A chemical analysis of the primary cations of interest (Na^+, K^+, Ca^{2+} and Mg^{2+}) was performed on PB+GW with an initial Na^+ concentration of 500 mg/L or 21.75 meq/L (PB+GW(500)). The concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} found in the initial and BRZ and BRZ(1M) sorption solutions were analyzed using ICP-OEC and are shown in Figure 2.11(A). Adsorption of Na^+, K^+, and Mg^{2+} to BRZ was observed with a removal percentage of 58%, 74%, and 11% respectively. Calcium appears to have been released from BRZ with approximately 14.6 meq/L Ca^{2+} desorbed; further analysis would have to have been conducted to determine the other cations released from the zeolite framework during adsorption. The suggested selectivity sequence of primary cations for BRZ is $K^+ > Na^+ > Mg^{2+} \approx Ca^{2+}$. BRZ(1M) adsorbed Na^+ and K^+ with removal efficiencies of 75% and 87% respectively; the concentration of adsorbed Na^+ and K^+ was 15.4 and 5.8 meq/L respectively. Chemical analysis suggested BRZ(1M) released Ca^{2+} and Mg^{2+} (to a lesser degree) which suggests that although protonation occurred, H^+ did not completely occupy the exchange sites prior to batch experiments. Analysis of the cation concentrations (supplementary data, Table 2.12) in Figure 2.11(A) shows that the release of unknown ions was approximately 180 mg/L and 400 mg/L for BRZ and BRZ(1M) respectively; it is believed that majority of this variance would be H^+ ions released from acid treated zeolite, resulting in an acidic effluent solution.

The ability of zeolite to reduce SAR of the initial PB+GW(500) was also investigated, with graphical representation shown in Figure 2.11(B). The measured concentrations of Na^+, Ca^{2+} and Mg^{2+} observed for the initial PB+GW(500) solution produced a SAR of 12.9. The BRZ and BRZ(1M) adsorbents were able to significantly reduce the SAR of the initial PB+GW solution to 2.7 and 1.9 respectively ($p \leq 0.001$).

Figure 2.11(C) shows the aluminum ion concentration for the PB+GW(500) as well as the sorption solutions for BRZ and BRZ(1M). The change in Al^{3+} concentration after adsorption was insignificant with the BRZ adsorbent ($p > 0.05$); however a significant difference was observed for BRZ(1M) ($p \leq 0.0001$). The Al^{3+} concentration increased during batch adsorption with BRZ(1M) from 0.002 meq/L for PB+GW(500) to 6.8 meq/L; this difference suggests that the Al^{3+} leached from the zeolite as a result of dealumination caused by acid treatment.





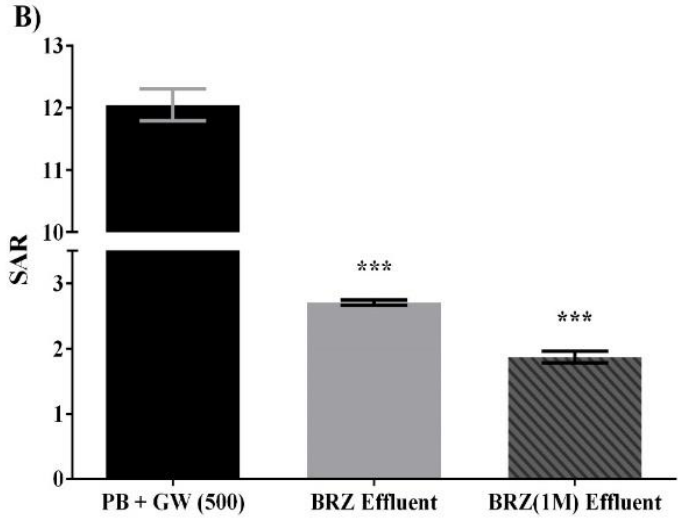


Figure 2.11: The adsorption and desorption of competing ions Na^+, Ca^{2+}, Mg^{2+} and K^+ from PB+GW(500) with an initial Na^+ concentration of 21.8 meq/L (A). Analysis of SAR(B) aluminum concentrations (B) for the initial PB + GW (500) solution (pH=7.95 ± 0.07) and BRZ (pH=7.33 ± 0.04) and BRZ(1M) (pH=2.48 ± 0.08) sorption solutions. Values represent the mean results and standard deviation.

2.5 Discussion

2.5.1 Sodium Sorption from Synthetic Solutions

2.5.1.1 Natural Zeolites

Adsorption behavior is influenced by many factors including cation exchange capacity, mineralogical purity, cations (exchangeable) pre-existing on adsorption sites and solid to liquid ratio (Inglezakis et al., 2002; Widiastuti et al., 2011). The initial Na^+ concentration inversely affects the zeolite sorption efficiency which is likely due to the decreasing quantity of available exchange sites as concentration of ions increases. Batch adsorption experiments produced adsorption capacities following BRZ>>SCZ≥CMZ, as shown in the isotherm in Figure 2.4.

It is believed that the limited active exchange sites caused by low CEC, initial exchangeable ions and mineralogical purity, could attribute to CMZ's sorption behavior. The success of adsorption processes is highly dependent on the presence of active exchange sites (Günay et al., 2007). The number of adsorption sites (CEC) for CMZ was the lowest among natural zeolites and available exchange sites would have been further limited by large proportions of K^+ and Na^+ initially present on the framework. The K^+ ions are selectively preferred over most other cations by clinoptilolite (Wajima, 2013), while, the exchangeable Na^+ content limited the available exchange sites required for Na^+ reduction. CMZ was found to be approximately 70% clinoptilolite-rich. It has been suggested that inactive adsorption sites may be associated with the presence of other minerals (impurities) (Curkovic et al., 1996; Inglezakis et al., 2001).

The batch adsorption experiments suggested that the sorption capacity for Na^+ of BRZ was almost twice that of CMZ and SCZ. An abundance of exchangeable Ca^{2+} and K^+ was measured on the zeolite framework. It is anticipated that the K^+ will occupy stronger adsorption sites; however, the Ca^{2+} ions will likely be easily exchangeable and located on weaker adsorption sites (Zhao et al., 2008). The mineralogical purity of BRZ (approximately 85% clinoptilolite) suggests the clinoptilolite-rich framework would likely have preferred Na^+ (Mumpton, 1999) and have a higher proportion of active adsorption sites accessible (Inglezakis et al., 2001). The CEC for BRZ was the highest among natural zeolites, which combined with the exchangeable Ca^{2+} content, can potentially explain its superior sorption behavior.

Previous adsorption studies have evaluated the effects of adsorbent mass to volume of solution (exposure of target ions) ratios for sodium (Belbase et al., 2013) as well as heavy metals (Inglezakis et al., 2004; Oren and Kaya, 2006). However, it was necessary to investigate the effects of m/V ratios on Na^+ uptake by BRZ, CMZ and SCZ. The m/V ratios were chosen based on previous findings suggesting lower m/V ratios (0.1 to 0.5) achieved higher sorption efficiency (Zhao et al., 2009; Wajima et al., 2010; Xu et al., 2010), likely due to greater adsorption densities and low aggregate formation which minimizes limitations of intra-particle and pore diffusion of Na^+ (Santiago et al., 2016). Adsorption isotherms were generated for BRZ, CMZ and SCZ at mass to volume ratios of 0.17 (Figure 2.4), 0.25 (Figure 2.13) and 0.5 (Figure 2.14); by comparing the maximum Na^+ sorption capacity for BRZ (Table 2.5), it is likely that sorption for Na^+ was not largely influenced at the m/V ratios studied. The influence of ratio variation on the performance of 1M H_2SO_4 pre-treated zeolite was not evaluated in this study; however, previous studies reported the use of m/V ratios less than 0.3 for acid treated zeolites (Xu et al., 2010; Wang et al., 2012). In this study, a m/V ratio of 0.17 was selected based on the sodium adsorption potential and optimized economic value (treating higher solution volume with same adsorbent mass).

2.5.1.2 Acid Treated Zeolites

Chemical (acid) treatment introduced a singular cation, H^+, to create a higher amount of exchange sites with more easily removable exchangeable cations, thus increasing the zeolite's sorption capacity, while minimizing structural framework damage. Modification with strong acids (such as H_2SO_4) has been suggested to enlarge the pore system and improve adsorption capacity (Liu and Yan, 2000). High concentrations of strong acids have been suggested to promote structural destruction (Garcia-Basabe et al., 2010). Framework damage may have been a reason for the insignificant increase in BET-N_2 surface area from BRZ(1M) and BRZ(2M), when compared to the significant difference between BRZ(0.1M) and BRZ(1M). Based on previous findings and preliminary Na^+ sorption results, 1.0M H_2SO_4 was used in this study.

Acid treatment altered the exchangeable ions present on the zeolite, generating protonic exchange sites which appeared to enhance sodium removal. The comparison of Na^+ removal from natural and acid treated zeolites (BR and CM) shows increased Na^+ uptake by BRZ(1M) and CMZ(1M) over their natural counterparts at the lower range of initial Na^+ concentrations. Previous studies reported the increase in cation adsorption capacity for acid treated zeolites was due to improved

exchange capacity, surface area and Si/Al ratio (Haldun Kurama et al., 2002; Rivera et al., 2013). The increase in CEC for BRZ(1M) compared to BRZ, suggests the number of available exchange sites increased, which has been reported to improve overall adsorption capacity (Bolan et al., 2003; Salvestrini et al., 2010). Another important factor was the nitrogen-BET surface area which appeared to increase with acid treatment, offering a larger surface area for ion exchange (Christidis et al., 2003; Li et al., 2011). The surface area increase of acid treated zeolites may be caused by the formation of more channels, cracks, cavities, and micropores, as well as the removal of fine particles which could clog pores (Jozefaciuk, 2002). Scanning electron microscopy images presented in Figure 2.12 in the supplementary data also suggest an increased surface area for BRZ(1M). XRF analysis suggested a slight increase in Si/Al ratio after acid treatment; previous studies suggest higher adsorption capacity and lower diffusional resistance (Panayotova, 2001; Öztaş et al., 2008) for zeolites exhibiting a higher Si/Al ratio.

Acid treatment causes a high degree of surface protonation, thus, breaking Al-O bonds on the aluminiosilicate surface and allowing for aluminum ions to leach from the zeolite framework (dealumination) (Xu et al., 2014). Dealumination occurred as a result of 1M H_2SO_4 treatment; verification can be seen by comparing the Al^{3+} contents of BRZ and BRZ(1M), visually in Figure 2.7 (blue) and numerically from the chemical analysis of sorption solutions (Figure 2.11(C)) and the Si/Al ratios. A portion of the aluminum ions reside in tetrahedral sites, thus, extensive removal of Al^{3+} could lead to interlayer disconnection and structural damage of the aluminiosolicate surface (Garcia-Basabe et al., 2010). It has been suggested that the stability of the dealuminated zeolite framework is related to the mineralogical purity and Si/Al ratio (Rivera et al., 2013). To minimize framework damage, acid treatment should only be applied for acid-stable zeolites (high Si/Al ratio) such as clinoptilolite (Breck, 1984; Wang et al., 2016), rather than chabazite or phillipsite which have low Si/Al ratios (Si/Al $\leq$ 4) (Salvestrini et al., 2010). The clinoptilolite component of BRZ and BRZ(1M) varied insignificantly, suggesting 1M H_2SO_4 treatment did not affect the mineral purity of zeolite; previous studies noted similar results for acid treated clinoptilolite (Li et al., 2008; Wang et al., 2012). Analysis of the sharpness and position of peaks was not provided in this study, thus, suggestions of minimal structural damage can only be inferred based on BRZ's high Si/Al ratio (6.2) and natural clinoptilolite purity (85.6%).

2.5.2 Influence of Competing Ions

Potash brine contamination could have profound negative impacts on surrounding ecological systems (Thorpe and Neal, 1991; Mohamed et al., 2005) as considerable Na^+ and K^+ would be present in water sources, along with Ca^{2+} and Mg^{2+} from naturally hard groundwater (Canada, 1979). The natural (BRZ and CMZ) and acid treated (BRZ(1M)) zeolites had reasonable success adsorbing Na^+ from synthetic sodium solutions; however, it was important to study this relationship in the presence of adsorption site competition. Batch adsorption experiments evaluated Na^+ sorption from PB+GW solutions. The Na^+ adsorption from PB+GW by CMZ was significantly impacted by the presence of alternative cations; the Na^+ removal percentage was consistently below 10% for all Na^+ concentrations and the maximum adsorption capacity was approximately 1.7 mg/g. A possible explanation is that the adsorption process was limited by the number (CEC), natural exchangeable ions, and proportion of fines, as well as accessibility of active exchange sites with selective cations adsorbing preferentially. The presence of competitive ions in the PB+GW negatively influenced Na^+ uptake for BRZ and BRZ(1M), although to a lesser degree than CMZ. This is likely attributed to the larger number of adsorption sites associated with higher CEC's of BR zeolites which lessens the negative impact of selective adsorption.

Clinoptilolite-rich zeolites exhibit ion selectivity based on cation valence charge, molecular size and hydration degree of the cation, as well as the Si/Al ratio of the zeolite (Cerri et al., 2002; Delkash et al., 2015). It was necessary to evaluate the affinity for Na^+, K^+, Ca^{2+} and Mg^{2+}, the primary exchangeable ions of concern in PB+GW. Chemical analysis of sorption solutions suggested removal of Na^+ and K^+ from the zeolite framework, in exchange for Ca^{2+} and small amounts of Mg^{2+}. The resulting adsorption selectivity for both natural and acid treated Bear River zeolites was observed to be $K^+ > Na^+ > Mg^{2+} \approx Ca^{2+}$, suggesting the H_2SO_4 treatment on the zeolite did not alter the zeolites adsorption selectivity in terms of K^+, Na^+ and Ca^{2+}. The cation preferential sequence was supported by chemical analysis on the sorption solutions, Figure 2.11(A). The ion exchange preference of Na^+ ions over Ca^{2+} ions on the clinoptilolite surface has also been suggested in previous studies (Dyer and Emms, 2005; Lei et al., 2008; Wajima et al., 2010). The high Si/Al ratio for clinoptilolite-rich zeolites (BRZ) likely resulted in a low electric field and a higher affinity for lower electrical charge densities such as those associated with monovalent cations (Cerri et al., 2002).

Long term soil exposure to irrigation water with a very high SAR (SAR≥13 (Agriculture, 2008)) can be detrimental to soil quality (Daliakopoulos et al., 2016). Implications of high SAR include deterioration of soil infiltration, permeability and aggregate stability, thus, making it unsuitable for vegetation growth (Warrence et al., 2003; Mohamed et al., 2005; Huang and Natrajan, 2006). Acid treated zeolites have been known to increase SAR after sorption because modification often exchanges Ca^{2+} for H^{+} on zeolite adsorption sites (Wang et al., 2012). The incomplete protonation achieved in this study, allowed for SAR reduction following PB+GW adsorption experiments with BRZ(1M). Complete protonation may have increased Na^{+} sorption capacity; however, this would have reduced the SAR of the sorption solution. The presence of competitive ions in PB+GW reduced Na^{+} uptake for BRZ and BRZ(1M); however, they were able to lower the SAR of the PB+GW(500), below the acceptable limit of four for 'unrestricted water use for agriculture purposes' (Abrol et al., 1988; Canada, 2000).

2.5.3 Evaluating Zeolite Performance

This study evaluated sodium sorption using multiple natural and acid treated zeolite adsorbents. This study suggested BRZ removed approximately 50% more Na^{+} than CMZ or SCZ due to optimized physiochemical characteristics. Sorption results suggest that the exchangeable ions and cation selectivity both played an important role in understanding ion exchange; BRZ contained significant proportions of exchangeable Ca^{2+} which should have exchanged with Na^{+} based on preferential ions. Evaluation of CMZ's properties suggest that CMZ would benefit from a pre-treatment technique to reduce the content of Na^{+} present on exchange sites naturally.

In this study, Figure 2.11(A) suggests protonation of the acid treated zeolite was incomplete due to the presence of exchanged Ca^{2+} ions in BRZ(1M)'s sorption solution. Future studies could be employed with a longer acid-treatment contact time or higher dosage, to determine the effects of homoionic conditions on zeolite properties and Na^{+} uptake. The acid treated zeolites obtained higher Na^{+} uptake than the natural zeolites at lower initial Na^{+} concentrations; however both adsorbents were able to treat the saline solutions (synthetic and PB+GW) to within an Aesthetic Objective (AO) of 200 mg/L (Canada, 2014). The Na^{+} uptake from BRZ and BRZ(1M) fit within the AO at initial Na^{+} concentrations of 500 mg/L (21.8 meq/L) and 750 mg/L (32.6 meq/L) respectively.

Drinking water standards suggest solution pH should be within 6.5 to 9.0 (Agency, 2015); the pH response from natural zeolite sorption solutions is within the desired range. The measured pH from sorption solutions with acid treated zeolite adsorbents was approximately 1.5 to 2.5, depending on acid concentration and solution type. Further experimentation is suggested to evaluate the effects of a neutralizing agent, such as lime or fly ash, on sorption solution pH and any potential effects on Na^+ sorption. The improved sorption capacity suggests that finding a neutralizing agent may make acid treated zeolites viable at low initial Na^+ concentrations (less than 43.5 meq/L or 1,000 mg/L).

Due to the laboratory scale of this study, zeolite material was obtained singularly from each mine. The zeolites studied were naturally formed minerals, therefore, would be subject to an undetermined level of variability. Future studies should evaluate the influence natural variability of the zeolite minerals has on sodium removal and the associated sorption-influencing properties.

2.5.3.1 Potential Applications

Zeolites are eco-friendly due to the exchangeable cations present in the zeolite structure which are harmless to nature (Gaikwad et al., 2011). The permeability of the material is an important parameter for future applications. Regulations suggest that a compacted clay liner for containment should have a saturated hydraulic conductivity less than or equal to 1.0×10^{-9} m/s (CCME, 2006). In this study, the hydraulic conductivity of natural BR zeolite (4.3×10^{-8} m/s) was not low enough to meet regulations; however, it could be decreased by mixing the zeolite with a more impermeable clay, such as bentonite. Previous studies have used Turkish zeolites and Na-bentonites for sorption of metals; results suggested sufficiently low hydraulic conductivity of the mixture(Kayabali, 1997; Tuncan et al., 2003; Yukselen-Aksoy, 2010). Bentonite typically has a lower CEC than zeolite; however, it has been suggested that mixing it with zeolite increases the CEC and maximum cation adsorption capacity of the liner (Tuncan et al., 2003; Turan and Ergun, 2009). Natural zeolite has the potential to be useful in preventing contaminant spreading due to its high sorption capacity, suitable plasticity, chemical stability and mechanical strength (Misaelides, 2011). The properties of zeolite adsorption for salinity mitigation from potash brine impacted groundwater, suggest its potential use as a filter media (pump and treat alternative) or secondary containment measure in conjunction with permeable reactive barriers (Oren and Ozdamar, 2013) or impermeable liners (zeolite-bentonite mixture) (Yukselen-Aksoy, 2010). Future studies could be employed to evaluate

the sodium sorption potential from BRZ-bentonite mixtures, including the sorption properties of the clay combination.

2.5.3.2 Natural Zeolite Feasibility

A material feasibility study was performed as a tertiary evaluation tool for natural BRZ and CMZ adsorbents to support decisions made based on sodium sorption as well as physiochemical properties. As this study does not encompass application design, the feasibility analysis focuses on the costs associated with zeolite, as well as freight shipping estimates with shipping to Saskatoon, Saskatchewan. A feasibility comparison of BRZ and CMZ is itemized in the supplementary data, in Table 2.14; this analysis includes material cost (in Canadian funds), as well as freight shipping estimates. Bear River Zeolite Co. mines zeolite near Preston, Idaho, USA but they currently have a Canadian distribution facility in Lethbridge, Alberta, Canada where bulk natural zeolite can be purchased for $0.30 per kilogram. The Canadian Mining Company Inc. mines their product at the Bromley Creek Zeolite Mine near Kamloops, British Columbia, Canada and can be purchased for $0.31 per kilogram. Analysis of the material cost and freight shipping charges produces a cost per kilogram of $2.30 and $2.20 for BRZ and CMZ respectively. The variance in cost, does not compensate for the difference in Na^+ sorption capacities for BRZ and CMZ suggested in this study. Table 2.6 includes the total material cost to treat 21.8 meq/L (500 mg/L) Na^+ solutions by BRZ using the Na^+ adsorption capacity obtained from the synthetic and PB+GW studies. The cost per liter to treat synthetic solutions and PB+GW was calculated at $0.08/L and $0.18/L respectively. The theory and calculations used to determine the cost per litre is presented in the supplementary data.

Table 2.6: Estimated material feasibility to treat synthetic Na^+ solutions and PB+GW with an initial Na^+ concentration of 21.8 meq/L. Material costs are detailed in Table 2.14.

	q_e (mg Na^+ / g zeolite)	**Zeolite Cost ($ / kg)**	**Total Cost ($ / L)**
Synthetic Na^+ Soln.	14.3	2.30	0.08
PB + GW	6.5		0.18

Deep well injection into a naturally saline aquifers is a popular alternative management practice for saline solutions (Mohamed et al., 2005), including within the potash industry (Vonhof, 1975). A feasibility study conducted by F. Huang and P. Natrajan (2006), suggested improving the Na^+

sorption capacity would reduce the cost to treat coal bed natural gas produced water, producing a competitive cost alternative to deep well injection ($0.75 to $4 per barrel). The interpolation of their feasibility study with the improved Na^+ sorption capacity by BRZ is shown in Table 2.15 in the supplementary data. The use of BRZ would have reduced the cost per barrel, making zeolite ion exchange a viable alternative (Huang and Natrajan, 2006). The use of BRZ to treat Na^+ contaminated solutions, could also be more feasible with the consideration of regenerating or recycling the sodium-saturated media.

2.6 Conclusion

This study suggests an ion exchange process with clinoptilolite-based zeolites as a successful salinity mitigation method. Of the natural zeolites studied, the zeolite obtained from Bear River Zeolite Co. showed superior adsorption capacity for sodium due to its calcium dominated exchange sites, effective cation exchange capacity and mineralogical purity. Attempts to optimize the adsorption capacity of natural zeolite through acid modification, increased the sodium removal at low initial Na^+ concentrations; however, this improvement is suggested to be impractical due to the acidic conditions created in the sorption solutions after exposure to the acid treated zeolites. Future studies could be useful for evaluating an oxidizing agent as BRZ(1M) suggested significant Na^+ adsorption potential over BRZ (less than 43.5 meq/L or 1,000 mg/L).

To simulate potential practical applications, adsorption studies were conducted using potash brine spiked groundwater samples. Chemical analysis of these batch adsorption studies suggested a preference of sodium over calcium ions on the zeolite framework. The presence of potassium ions in the potash brine reduced the sodium adsorption potential; however, the Na^+ removal reduction was limited to 10% or less.

The current local distribution partnership for Bear River Zeolite Co. provides feasibility support, which combined with its enhanced sodium sorption capacity, suggests natural BRZ as the most viable zeolite adsorbent considered in this study, for saline solutions. Ion exchange with BRZ is a potential salinity mitigation method due to its low hydraulic conductivity, cost effectiveness, local and worldwide availability, and eco-friendly ion exchange process. The feasibility of natural zeolites may be further improved through the investigation of regeneration techniques to extend its lifespan.

2.7 Supplementary Data

2.7.1 Material Characterization

Table 2.7: Complete solution chemistry results for potash brine, groundwater and brine spiked groundwater (PB + GW (500)) measured by SRC Environmental Analytical Laboratories.

Parameter	Potash Brine	Groundwater	PB + GW (500)
Aluminum (mg/L)	0.76		<0.005
Antimony (mg/L)	<0.02		
Arsenic (mg/L)	13		
Barium (mg/L)	0.82		
Beryllium (mg/L)	<0.01		
Bicarbonate (mg/L)	73	461	443
Boron (mg/L)	<1.0		
Cadmium (mg/L)	<0.001		
Calcium (mg/L)	2000	111	49
Carbonate (mg/L)	<1.0	<1	<1
Chloride (mg/L)	219000	14	1060
Chromium (mg/L)	0.17		
Cobalt (mg/L)	<0.01		
Copper (mg/L)	0.75		
Hydroxide (mg/L)	<1.0	<1	<1
Iron (mg/L)	0.8	0.27	0.018
Lead (mg/L)	<0.01		
Magnesium (mg/L)	1800	32	40
Manganese (mg/L)	3.0		
Molybdenum (mg/L)	0.04		
Nickel (mg/L)	0.12		
Nitrate (mg/L)	<0.04	<0.04	0.15
Potassium (mg/L)	58200	3	258
Selenium (mg/L)	0.13		
Silicon (mg/L)			6.2
Silver (mg/L)	0.009		

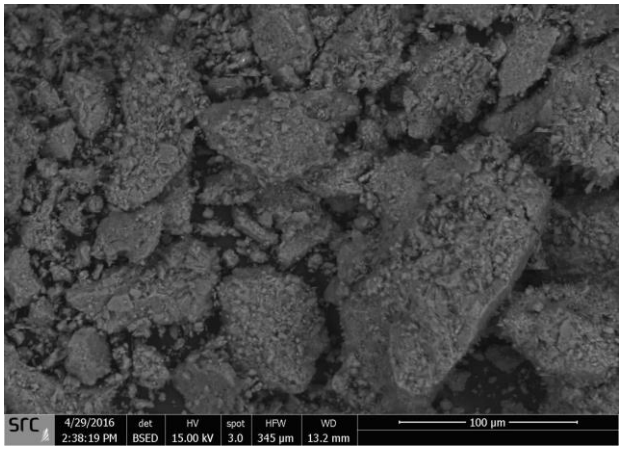
Sodium (mg/L)	89500	12	469
Strontium (mg/L)	35.7		
Sulfate (mg/L)	1800	30	39
Thallium (mg/L)	<0.02		
Tin (mg/L)	<0.01		
Titanium (mg/L)	<0.02		
Uranium (mg/L)	<10		
Vanadium (mg/L)	0.01		
Zinc (mg/L)	0.25		
Total Alkalinity (mg/L as $CaCO_3$)	60		
pH	7.22	8.34	7.95
Specific Conductivity (µS/cm)	242000		
Total Dissolved Solids, TDS[1] (mg/L)	372373	663	2426
Total Hardness (mg/L as $CaCO_3$)	12380	409	457
SAR	350	0.26	9.55

[1] – TDS = Cl^- + SO_4^- + Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NO_3^- + CO_3^{2-} + HCO_3^-

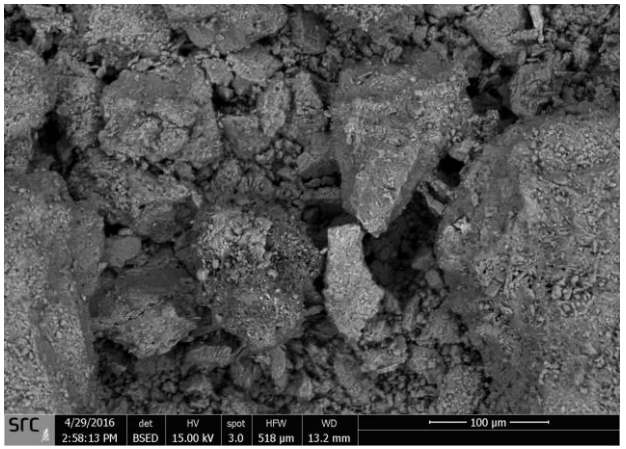
Table 2.8: XRD analytical results for BRZ, BRZ(1M) and CMZ.

Zeolite Sample	Haulandite-Ca (%)	Heulandite-K (%)	Illite (%)	Quartz (%)	Cristobalite (%)
BRZ	61.9	23.7	2.8	2.2	9.4
CMZ	61.6	7.7	19.5	0.5	10.8
BRZ(1.0M)	74.6	11.5	3.2	2.9	7.7

(A)



(C)



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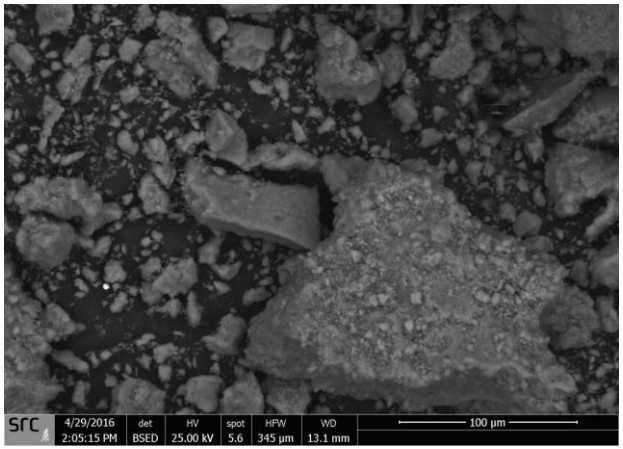


Figure 2.12: SEM images of natural BRZ (A), CMZ (B) and acid treated BRZ(1M) (C) prior to sorption experiments.

2.7.1.1 Hydraulic Conductivity Determination

Darcy's Law was used as a basis for calculating the hydraulic conductivity, *k* (m/s):

$$Q = -kAi = -kA\frac{\partial h}{\partial l} \tag{2.7}$$

where Q is the flow rate (m^3/s), *k* is the hydraulic conductivity (m/s), A is the cross sectional area of the sample and *i* is the hydraulic gradient or change in hydraulic head over a distance. BRZ permeability experiments were conducted in triplicate, according to the falling head method and calculated using Equation 2.8:

$$k = \frac{2.3aL}{A\Delta t}\log\left(\frac{h_1}{h_2}\right) = \frac{aL}{A\Delta t}\ln\left(\frac{h_1}{h_2}\right) \tag{2.8}$$

where a is the cross-sectional area of the water containing burette (m^2), L is the length of flow (m) and Δt is the change in time (s).

2.7.2 Additional Sodium Sorption Results

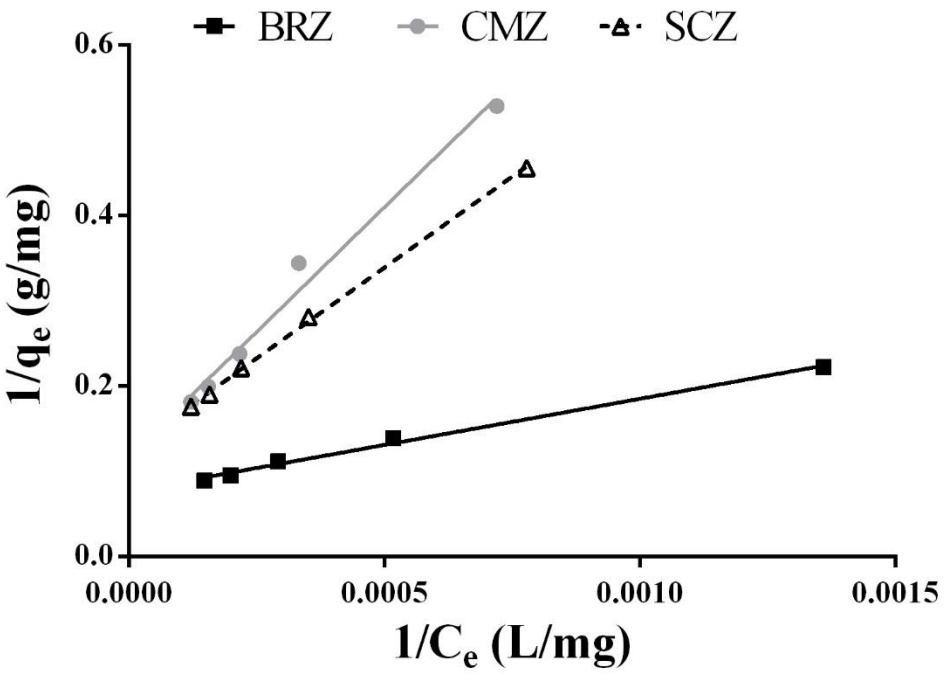


Figure 2.13: Langmuir isotherm analysis of BRZ, CMZ and SMZ data from batch adsorption experiments with a mass to volume ratio of 0.25.

Table 2.9: Isotherm model parameters from the non-linear squares analysis for batch adsorption experiments conducted on BRZ, CMZ and SCZ at a mass to volume ratio of 0.25.

Model	Parameters	*BRZ*	CMZ	SCZ
Langmuir	q_e (mg/g)	13.8 ± 0.6	10.0 ± 1.1	8.2 ± 0.2
	K_L	0.0006 ± 0.00007	0.0002 ± 0.00006	0.0003 ± 0.00001
	R^2	0.991	0.990	0.999
	Sy.x	0.30	0.17	0.05
Freundlich	K_F [(mg/g)(L/mg)$^{1/n}$]	0.35 ± 0.07	0.02 ± 0.01	0.07 ± 0.02
	n	2.5 ± 0.2	1.7 ± 0.1	2.0 ± 0.1
	R^2	0.991	0.986	0.989
	Sy.x	0.29	0.20	0.17
Δ AIC		0.01	-1.50	-11.57
Evidence Ratio		1.0	2.1	325
Preferred Model		Freundlich	Langmuir	Langmuir

± – corresponds to the standard error

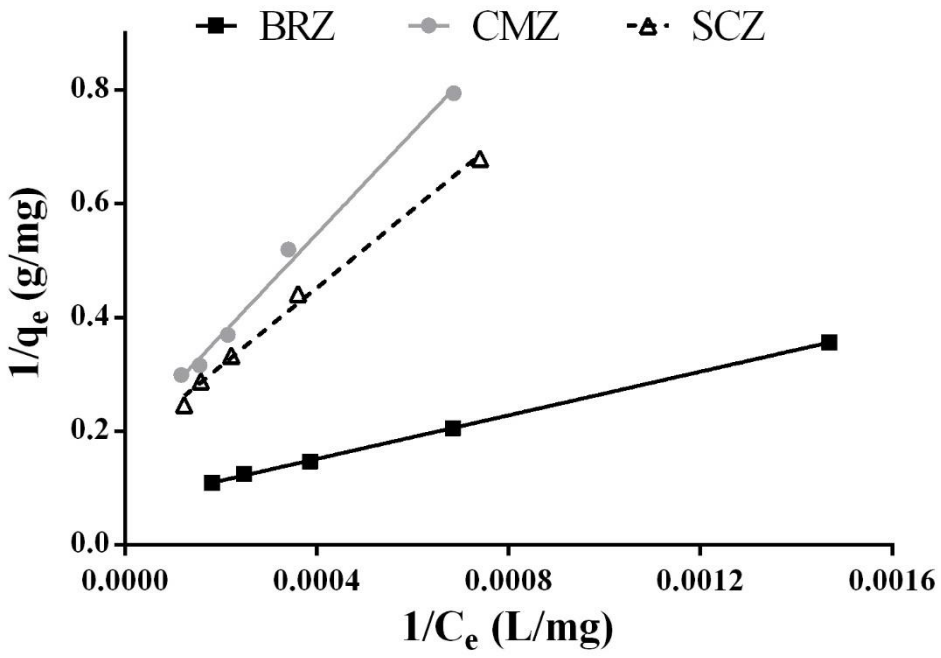


Figure 2.14: Langmuir isotherm analysis of BRZ, CMZ and SMZ data from batch adsorption experiments with a mass to volume ratio of 0.5.

Table 2.10: Isotherm model parameters from the non-linear squares analysis for batch adsorption experiments conducted on BRZ, CMZ and SCZ at a mass to volume ratio of 0.50.

Model	Parameters	*BRZ*	CMZ	SCZ
Langmuir	q_e (mg/g)	13.3 ± 0.4	5.4 ± 0.4	6.3 ± 0.4
	K_L	0.0004 ± 0.00003	0.0002 ± 0.00003	0.0002 ± 0.00003
	R^2	0.998	0.990	0.992
	Sy.x	0.12	0.11	0.10
Freundlich	K_F [(mg/g)(L/mg)$^{1/n}$]	0.11 ± 0.04	0.03 ± 0.01	0.03 ± 0.01
	n	1.9 ± 0.2	1.9 ± 0.2	1.8 ± 0.1
	R^2	0.984	0.972	0.998
	Sy.x	0.36	0.17	0.06
Δ AIC		-10.82	-5.11	5.79
Evidence Ratio		223	12.9	18.0
Preferred Model		Langmuir	Langmuir	Freundlich

± – corresponds to the standard error

Table 2.11: The maximum adsorption capacities, q_e, for BRZ, CMZ and SCZ at mass to volume ratios of 0.17, 0.25 and 0.5.

q_e (mg/g)	0.17	0.25	0.5
BRZ	14.3 ± 0.4	13.8 ± 0.6	13.3 ± 0.4
CMZ	5.8 ± 0.5	10.0 ± 1.1	5.4 ± 0.4
SCZ	5.6 ± 0.7	8.2 ± 0.2	6.3 ± 0.4

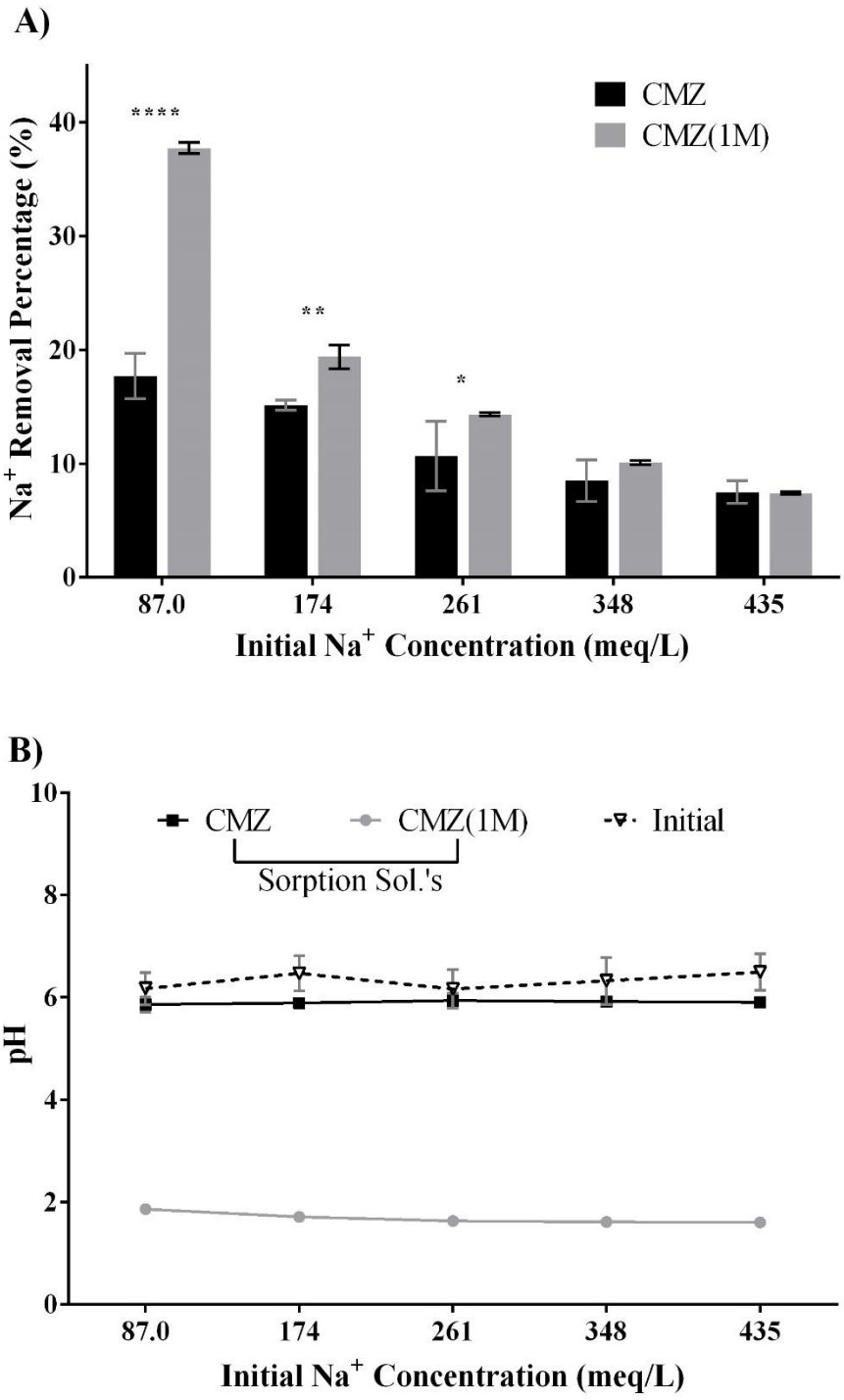


Figure 2.15: Evaluating the effect of 1M H_2SO_4 treatment on sodium uptake for (A) Canadian Mining zeolites at an m/V ratio of 0.17. The average pH responses of the adsorption effluents in comparison to the initial sodium solution pH for CMZ and CMZ(1M) (B). Values represent the mean results and standard deviation.

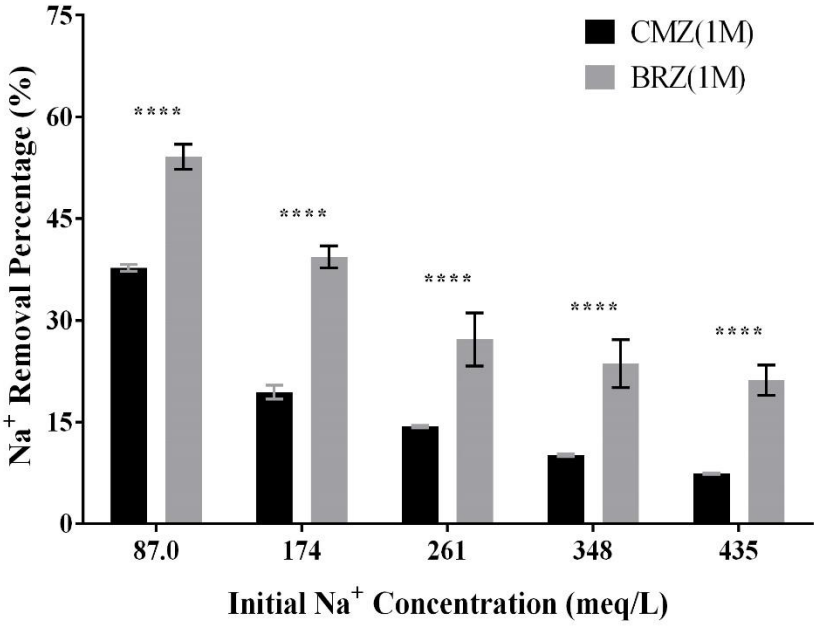


Figure 2.16: Using synthetic sodium solutions to evaluate Na^+ uptake of acid (1M H_2SO_4) treated zeolites, BRZ(1M) and CMZ(1M). Values represent the mean results and standard deviation.

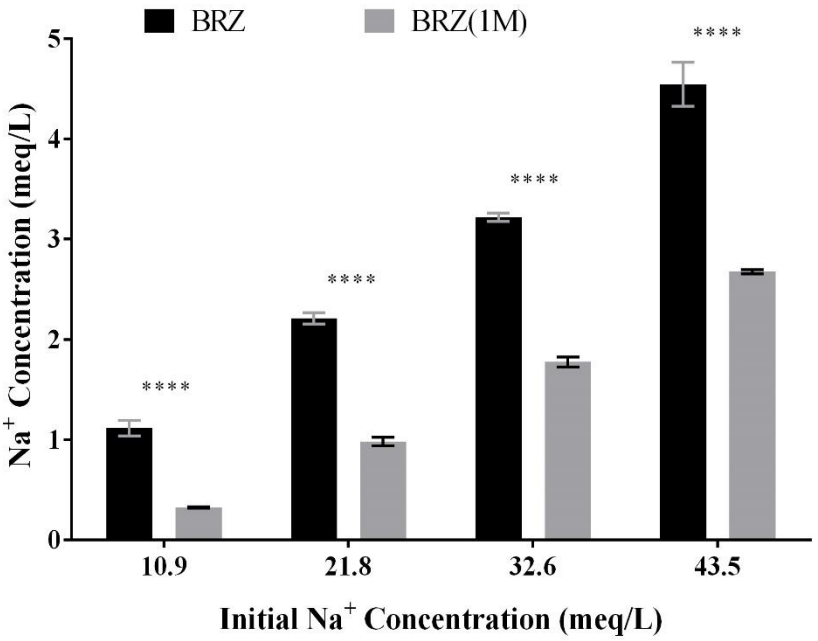


Figure 2.17: Comparing desorption of Na^+ ions from BRZ and BRZ(1M) after undergoing batch adsorption with sodium solutions and reusing zeolite for sorption experiments with DI water. Values represent the mean results and standard deviation.

Table 2.12: Water chemistry of PB + GW(500) and resulting solutions from sorption experiments with BRZ and BRZ(1M).

	PB + GW (500)		BRZ		BRZ(1M)	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Na^{+}	470	20.44	196.7	8.56	116.7	5.08
Ca^{2+}	49	2.45	340	17.00	223	11.15
Mg^{2+}	40.3	3.30	35.3	2.89	41.3	3.39
K^{+}	260	6.65	68.7	1.76	32.7	0.84
Al^{3+}	0.019	0.0021	0.006	0.00067	61	6.79
Si^{4+}	6.57	0.94	18	2.56	32.7	4.65
T. Hardness (as $CaCO_3$)	287	5.74	995	19.88	728	14.55
SAR	12.07		2.71		1.88	

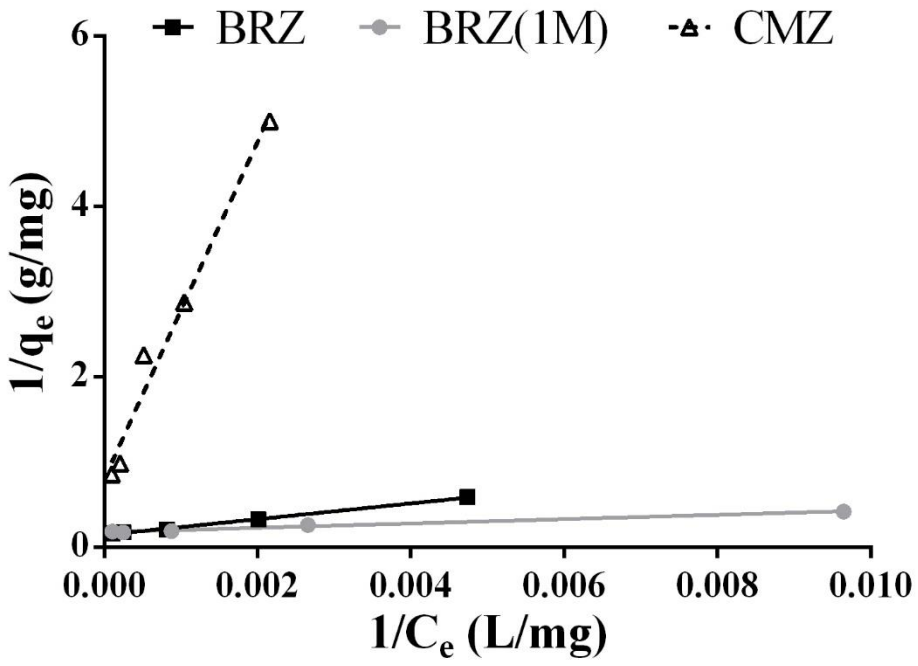


Figure 2.18: Langmuir isotherm analysis of BRZ, BRZ(1M) and CMZ data from PB+GW batch adsorption experiments.

Table 2.13: Isotherm model parameters from the non-linear squares analysis for batch adsorption experiments conducted on BRZ, BRZ(1M) and CMZ with PB+GW solutions.

Model	Parameters	*BRZ*	BRZ(1M)	CMZ
Langmuir	q_e (mg/g)	6.5 ± 0.2	5.7 ± 0.2	1.7 ± 0.3
	K_L	0.0019 ± 0.0002	0.0065 ± 0.0012	0.0002 ± 0.00002
	R^2	0.992	0.970	0.969
	Sy.x	0.19	0.28	0.09
Freundlich	K_F [(mg/g)(L/mg)$^{1/n}$]	0.65 ± 0.34	1.60 ± 0.65	0.01 ± 0.01
	n	3.9 ± 1.0	6.9 ± 2.5	1.9 ± 0.3
	R^2	0.869	0.762	0.941
	Sy.x	0.77	0.78	0.12
Δ AIC		-13.94	-10.38	-3.11
Evidence Ratio		1065	180	4.7
Preferred Model		Langmuir	Langmuir	Langmuir

± – corresponds to the standard error

2.7.3 Cost Analysis Data

Table 2.14: Detailed cost analysis for BRZ and CMZ.

	Bear River	Canadian Mining
Material ($ / kg) [1]	$0.30	$0.31
Material Mesh Size	–40	–36
Std. Crate Mass (kg)	1,000	900
Distribution Center	Lethbridge, AB	Kamloops, BC
Shipping ($ per Crate)	$1,980	$1,695
Total Cost per Crate ($)	$2,280	$1,975
Total (CAD $)	**$2.30/ kg** [2]	**$2.20 / kg**

[1] – Cost is in Canadian funds (Nov. 2017) including taxes (GST and PST)
[2] – Canadian Distributor (shipping from mine in Preston, ID is $5.25/kg CAD)

The Canadian Mining Company Inc. provides their zeolite in bulk crates (approximately 900kg), sized to -36 Mesh for a price per kilogram of $0.31 (including taxes). The zeolite is mined at the Bromley Creek Zeolite Mine with material distributed from Kamloops, BC, Canada. Bear River Zeolite Co. mines their product near Preston, ID, USA but the company currently has a Canadian distribution center located in Lethbridge, AB, where bulk (one metric-ton) natural zeolite, sized to -40 Mesh, can be purchased for $0.30 per kilogram. The total cost per kilogram for the material and shipping for CMZ and BRZ is $2.20 and $2.30 respectively; the slight difference is due to the standard material mass which varies between companies as well as the route provided by FedEx. In the future, if the Canadian BRZ distribution ceases, the feasibility of BRZ becomes questionable: the price to ship BRZ to Canada is $5.25 per kilogram, assuming material costs, size and quantity remains consistent.

Table 2.15: The total cost estimates for BRZ and SCZ where synthetic solutions (initial Na^+ concentration of 21.5 meq/L) were used to determine the Na^+ sorption capacity.

	Sorption Capcity, q_e		Total Cost	
	meq / g	mg Na^+ / g z.	$ / barrel[2]	$ / L
BRZ	0.6	14.3	1.70	1.1×10^{-2}
SCZ [1]	0.1	2.2	3.00	1.9×10^{-2}

[1] – Experimental results using St. Cloud Zeolite Co. results from Huang and Natrajan (2006)
[2] – 1 barrel = 159 L

Huang and Natrajan (2006) conducted a feasibility study based on sorption experiments using zeolite obtained from St. Cloud Zeolite Co. Experiments were conducted at 20°C with 14x40 Mesh zeolite. The interpolated data is a result of the suggested cost a tenfold increase of the Na^+ sorption capacity, q_e, would yield; an increase in q_e from 0.1 to 1.0 meq/g, would result in a cost decrease from \$3.00/barrel to \$0.75/barrel (Huang and Natrajan, 2006). The suggested cost for deep well injection was \$0.75-4.00 per barrel for coalbed natural gas produced water; adsorption experiments using BRZ lower the cost to comfortably within the cost range of deep well injection.

Interpolation calculation:

q_e = 0.613 meq/g
q_i = 0.097 meq/g
q_f = 1.0 meq/g
C_e = unknown
C_i = \$3.00
C_f = \$0.75

$$C_e = \frac{(q_e - q_i) \times (C_f - C_i)}{(q_f - q_i)} + C_i = \frac{(0.613 - 0.097) \times (0.75 - 3.00)}{(1.0 - 0.097)} + 3.00 = \$1.70$$

3 – integrated treatment process using clinoptilolite-rich zeolite: sodium sorption and water softening cycles [2]

[2] This chapter was written in joint authorship with Dr. Wonjae Chang (academic supervisor). The experiments within this study were designed and completed by Ashley Siemens. The data analysis, computation and manuscript preparation was conducted by Ashley Siemens under the supervision of Dr. Wonjae Chang. Dr. Wonjae Chang is the Principal Investigator of the IMII research program in which this study is a part of. We gratefully acknowledge Helen Yin for her technical assistance in the Environmental Engineering Lab.

3.1 Abstract

Natural zeolites as ion exchange materials have been proven as a successful reclamation technique for many applications. Previous studies have focused on optimizing the exchange capacity of natural zeolites. One technique that has been proven effective is pre-treatment using alkaline earth metal cations, primarily sodium, to create near homoionic conditions on zeolite exchange surfaces. Previous studies have suggested differing cation selectivity preferences for sodium and calcium ions based on zeolite type and form. Reclamation of highly saline mine effluent solutions is a primary objective in this study, thus, pre-treatment with sodium cations is impractical. This study examined natural zeolites from British Columbia, Canada and Idaho, United States, to optimize the exchange and regeneration potential. Pre-treatment with a hard water solution, containing calcium and magnesium cations successfully improved sodium uptake. Preliminary experiments suggested the use of the Canadian-mined zeolite as an ion exchange media in a dual treatment process that combined hard water softening (Ca^{2+} and Mg^{2+} removal) and desalination (Na^{+} removal). The zeolite was first used to treat hard water, which produced Ca- and Mg-rich zeolites that increased Na^{+} removal by approximately 77%. This proposes a potential dual-treatment system (hard water softening and desalination) while extending the life cycle of the zeolite adsorbent.

3.1.1 Keywords

Zeolite, clinoptilolite, sorption, ion exchange, sodium removal, pre-treatment, regeneration, hard water treatment, water softening, calcium, magnesium

3.2 Introduction

A potential source of groundwater contamination is from the highly saline potash waste liquids. Potash mining extracts potassium which is primarily used for the production of fertilizer to promote plant growth (Marshall, 2015). Potash, or sylvinite, ore is mined from subsurface evaporite formations deposited millions of years ago (Hart, 1989). It is estimated that approximately half of the world's potash deposits are located in Canada; the majority of these reserves are in Saskatchewan which mines the sylvinite deposits of the Prairie Evaporite Formation (Jensen et al., 2006). Saskatchewan produces approximately one third of the world's potash supply (SMA, 2012; Rawashdeh and Maxwell, 2014). The mining of potash produces solid tailings and liquid brine consisting of approximately 90% sodium chloride (NaCl), 7-8 % potassium chloride (KCl) and trace amounts of insoloubles (Wong and Barbour, 1987). The volume of potash waste products produced per tonne of KCl refined has reduced as mining and extracting methods have improved (Tallin et al., 1990; PotashCorp, 2011; Mosaic, 2015); however, the production of potash mine waste products and their potential impact on the surrounding environment is still a significant concern. Currently, a portion of the brine is reclaimed into the mining process with the remainder being deposited in brine ponds where it either remains as residual liquid, naturally evaporates or is well injection into deep, naturally saline aquifers (Reid, 1984; Thorpe and Neal, 1991; Reid and Getzlaf, 2004). As liquids are typically more difficult to contain than solid waste products, extensively engineered systems have been designed to manage potash brine waste products and minimize potential environmental contamination concerns. The waste management system consists of lined ponds which are supported by dykes, impoundment walls, trenches, drainage ditches and capture wells (Hart, 1989). This system works to minimize the risk of contaminate migration into surrounding soil and water systems, primarily the extensive aquifer systems underlying many mine sites.

The potential migration of this highly saline brine into the surrounding environment is a significant concern due to the negative impacts that exposure to sodium can have on the physical and chemical properties of soil. High sodium levels do not directly limit water intake by plants; however, it does alter the soil's physical structure, causing soil dispersion which reduces its permeability and infiltration capacity, thus, impacting plant growth (Warrence et al., 2003; Mohamed et al., 2005). The dispersed soil conditions and low permeability also results in restricted root growth and

increased susceptibility to wind and water erosion (Bernstein, 1975; Seelig, 2000). The presence of soil salts also change the osmotic pressure of the water within the which reduces the amount of water available for uptake and causes nutrient deficiencies (Mau and Porporato, 2015). Poor soil structure caused by long term exposure to high sodium levels has profound impacts on agricultural production and environmental health, as well as socio-economic effects (Daliakopoulos et al., 2016). The wide-spread impacts associated with prolonged exposure to high sodium levels suggests the importance of developing economical and eco-friendly salinity remediation alternatives. Currently, desalination methods include reverse osmosis, multistage flash, electrodialysis and/or ion exchange technologies (Wajima, 2013). Ion exchange provides a more cost effective alternative to reverse osmosis (Chen et al., 2014).

A common water treatment technique is softening hard water; water hardness is caused by dissolved metallic cations, primarily calcium (Ca^{2+}) and magnesium (Mg^{2+}) and occasionally small amounts of iron and manganese (Park et al., 2007). The hardness of water is typically measured through a reaction with a chelating agent to determine the concentration of calcium and magnesium cations, as expressed in milligrams per liter equivalent of calcium carbonate ($CaCO_3$) (Freeze and Cherry, 1979). Hard water is not a health issue; however, in Saskatchewan, water hardness can be a significant concern with groundwater levels ranging from 40 to 1,300 mg/L as $CaCO_3$ (Canada, 1979). Groundwater is typically 'harder' than surface waters due to the presence of carbonates which in Saskatchewan, are primarily in the form of calcite and dolomite (Rostad and Arnaud, 1970). Water softening is traditionally employed for hardness levels near 200 mg/L as $CaCO_3$ (Saskatchewan, 2008). The vast range of hardness values measured for groundwater throughout the region suggested a practical or simulated approach be taken for determining the total hardness value for this study.

Unlike saline solutions, hard water does not have any significant health or environmental concerns; however, it does react with negative ions found in soap and detergents, adversely affecting their cleaning efficiency (Van Mao et al., 1994; Prasad et al., 2011). These reactions also cause the formation of deposits of hardness; many industrial and domestic water uses involve heating which would cause the creation of insoluble calcium carbonate to form from the naturally occurring calcium and bicarbonate ions found in hard water (Manahan, 2010). The insoluble mineral deposits can induce scaling problems, leading to mechanical failures associated with pipeline blockage,

membrane clogging and efficiency reduction in boilers, heater exchangers and common household electrical appliances (Gabrielli et al., 2006; Seo et al., 2010). Water hardness is commonly described as soft (0 to 60 mg/L as $CaCO_3$), medium hard (60 to 120 mg/L as $CaCO_3$), hard (120 to 180 mg/L as $CaCO_3$) and very hard (greater than 180 mg/L as $CaCO_3$) (Canada, 1979).

To avoid costly failures, water hardness is monitored and reduced when necessary; water softening describes the removal of hardness causing ions (Park et al., 2007). Water softening can be accomplished through a variety of processes such as chemical precipitation (phosphates and lime softening), membrane systems (reverse osmosis and nanofiltration), electromembrane systems (electrolysis, electrodialysis, electrodialysis reversal and electrodeionization reversal) and ion exchange resins (Manahan, 2010; Seo et al., 2010). Chemical precipitation consists of the addition of a chemical to promote carbonate precipitation; however, calcium and magnesium carbonates have a limited solubility, thus, hardness cannot be completely reduced with this method (Wood, 1972). The addition of chemicals must be closely monitored; polyphosphates used for chemical precipitation are successful for sequestering hardness ions; however, the phosphates discharged as a result, can cause negative environmental impacts such as eutrophication of surface waters (Xue et al., 2014). Lime softening uses lime ($Ca(OH)_2$) and soda ash (Na_2CO_3) to treat hard water, resulting in the precipitation of calcium and magnesium (Manahan, 2010). Lime soda plants do not require pre-treatment of water to reduce suspended materials; however, in comparison to zeolite ion exchange systems, it is more expensive for initial equipment costs, as well as disposal of the produced waste sludge (Wood, 1972). Membrane and electromembrane techniques avoid the use of potentially toxic chemicals (Gabrielli et al., 2006); however, they require high power consumption and are prone to membrane fouling, resulting in high operating and maintenance costs (Chen et al., 2014). Reverse osmosis (RO) and ion exchange both require pre-treatment filtration systems to eliminate the presence of suspended solids and organic matter; however, RO is also energy intensive, resulting in higher operating costs than ion exchange systems (Hughes and Crane, 1930; Chen et al., 2011). Ion exchange, using a natural material such as zeolite, has low initial and operating costs, high softening efficiency (reducing hardness essentially to zero), does not alter the organoleptic properties of the water and low chemical requirement (Hughes and Crane, 1930; Wood, 1972; Bibiano-Cruz et al., 2016). The removal of the primary hardness cations with zeolite has been proven successful (Arrigo et al., 2007; Prasad et al., 2011; Xue et al., 2014). The potential impacts associated with water hardness and salinity on soil and water quality require

an economical and environmentally friendly solution; ion exchange using zeolite adsorbents has gained popularity for water treatment due to those reasons, as well as it's ion exchange properties, worldwide availability and desirable catalytic, hydraulic, mechanical and thermal properties (Li et al., 2011; Misaelides, 2011).

Natural zeolites are hydrated, crystalline aluminosilicates of alkali and alkaline earth metals with SiO_4 and Al_3O_4 bound in a tetrahedral formation by shared oxygen atoms (Haldun Kurama et al., 2002; Santiago et al., 2016). Natural zeolites are associated with alkaline lake deposits and sedimentary rock formations formed through the alteration of volcanic ash (Kayabali, 1997). Approximately 40 natural zeolites have been identified, with the most common types being clinoptilolite, erionite, chabazite, mordenite and phillipsite, all of which have deposits in North America (Virta, 1997). Clinoptilolite is a heulandite-type zeolite (Öztaş et al., 2008; Wang and Peng, 2010), associated with sedimentary formations (Yukselen-Aksoy, 2010) and one of the most abundant of the naturally occurring zeolites (Breck, 1984; Wang et al., 2016). Clinoptilolite deposits are being mined via open pit mining methods (Virta, 1997) in British Columbia, Canada (Read, 1995) as well as six USA states: California, Idaho, New Mexico, Oregon, Texas and Wyoming (Virta and Phamdang, 2002). Clinoptilolite has been frequently used for water treatment (ion exchange) due to its adsorption selectivity preferences, cation exchange capacity, and low cost (Xu et al., 2014; Delkash et al., 2015).

The zeolite structure has a negative surface charge from the isomorphic substitution of Si^{4+} for Al^{3+} (Oren and Ozdamar, 2013). The negatively charged surface is balanced by exchangeable cations, such as Na^+, K^+, Ca^{2+} and Mg^{2+}, which are bound by electrostatic forces to the aluminosilicate structure (Ghaly and Verma, 2008; Widiastuti et al., 2011). The rigid, three-dimensional structure have a series of interconnected channels and voids, similar to a honeycomb (Oren and Ozdamar, 2013; Delkash et al., 2015). This extensive channel system, combined with their porous structure, results in large specific surface areas of the zeolite which aid in increasing its cation exchange ability (Vivacqua et al., 2013). The zeolite's open framework allows ions to filter through depending on channel size and configuration, as well as molecular size of the ion (molecular sieve) (Li et al., 2008; Yukselen-Aksoy, 2010). Ion exchange occurs as a result of a concentration gradient between solid and liquid phases, thus the diffusion of cations will occur until an equilibrium state is reached. The cation exchange capacity (CEC) is a measure of the

number of ions that can be adsorbed, through ion exchange, to the negative exchange sites on the zeolite surface (Erdem et al., 2004). Natural clinoptilolite-rich zeolites typically exhibit CEC's ranging from 60meq/100g to 230meq/100g (Wang and Peng, 2010). The exchange capacity depends on zeolite properties such as surface area, accessibility of exchange sites, mineral purity, Si/Al ratio and cation exchange capacity (Inglezakis et al., 2001; Cheng et al., 2005); experimental properties including initial ion concentration, contact time, solid to liquid batch adsorption ratio and presence of competitive ions in the sorption solution, can also influence ion exchange (Ganjegunte et al., 2011; Delkash et al., 2015). The adsorption behavior regarding cation selectivity mainly depends on factors related to the valence charge, field strength and hydration degree (ionic radius) of the cations present (Inglezakis et al., 2003; Cui et al., 2006). The suggested selectivity sequence for clinoptilolite-rich zeolites is $Cs>Rb>K>NH_4^+>Ba>Sr^{2+}>Na^+>Ca^{2+}>Fe^{3+}>Al^{3+}>Mg^{2+}>Li^+$ (Mumpton, 1999; Liu and Lo, 2001; Fu et al., 2011). However, the sequence regarding clinoptilolite's selectivity preference for Na^+ over Ca^{2+} has been inconsistent in previous studies with some studies suggesting the preference of Ca^{2+} over Na^+ cations (Curkovic et al., 1996; Arrigo et al., 2007; Xu et al., 2012), suggesting variation according to clinoptilolite type. Based on the primary author's research, a consensus has not been determined regarding the exchange preference for Na^+ and Ca^{2+} cations for clinoptilolite-rich zeolites, with it; however it suggests that exchange between the two cations, Na^+ and Ca^{2+}, should be achievable.

Ion exchange using zeolites results in the release of non-toxic alkaline and alkaline earth cations, which combined with the low technology requirements associated with these systems and inexpensive costs associated with zeolite production, provides an environmentally friendly and economically viable remediation alternative (Gaikwad et al., 2011; Widiastuti et al., 2011). Zeolite has been successfully used for ion exchange in many applications including agronomy, horticulture, and aquaculture, as well as the treatment of wastewater and mining waste products (Wajima, 2013). Natural clinoptilolite has been thoroughly investigated for the removal of heavy metal ions (Fe^{3+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, Fe^{2+} and Cd^{2+}) from industrial waste products (Inglezakis et al., 2002; Inglezakis et al., 2003; Wingenfelder et al., 2005; Oter and Akcay, 2007; Vidal et al., 2009), as well as ammonium ions for wastewater treatment (Liu and Lo, 2001; Karadag et al., 2006; Saltalı et al., 2007). Natural clinoptilolite-rich zeolites have also been used to adsorb cations associated with hard water, such as Ca^{2+} and Mg^{2+}; however, previous studies using zeolite ion exchange for water softening focused on hardness levels ranging from 200 to 400 mg/L as $CaCO_3$

(Chen et al., 2014; Ebrazi and Banihabib, 2015), which is lower than anticipated for practical applications within the region studied. Zeolite has also successfully adsorbed Na^+ ions from saline solutions such as seawater and coalbed natural gas co-produced waters (Taulis and Milke, 2007; Wajima et al., 2010; Belbase et al., 2013; Millar et al., 2016); these studies also tended to focus on lower concentration ranges.

Pre-treatment techniques have proven successful for increasing cation sorption capacity in zeolites through physical or chemical modification (Klieve and Semmens, 1980; Liang and Ni, 2009; Fu et al., 2011). Modification techniques commonly include the introduction of heat (Lei et al., 2008), surfactants (Bowman, 2003; Ghiaci et al., 2004), acids and/or alkaline earth metal cations (Wang et al., 2012). Chemical modification through the addition of concentrated acids (H^+) or alkaline metal cations (Na^+, Ca^{2+}, K^+ or Mg^{2+}) results in cation exchange within the zeolite framework, with exchange sites then being occupied by the introduced cation. The replacement cation traditionally is more removable for ion exchange applications and the increased presence of a singular cation, creates near homoionic conditions on the zeolite exchange sites (Günay et al., 2007). Acid modification introduces H^+ or protonic exchange sites and has been successful at increasing zeolites sorption capacity for ammonium (Bolan et al., 2003; Li et al., 2011), heavy metals (Günay et al., 2007; Gedik and Imamoglu, 2008; Xu et al., 2014) and sodium (Wang et al., 2012; Santiago et al., 2016). In Chapter 2, the study evaluated the influence of sulfuric acid (H_2SO_4) on sodium removal at varying concentrations and zeolite forms; results suggest improved Na^+ sorption for lower initial Na^+ concentrations. The acid treated zeolite which performed best in Chapter 2, was evaluated in this study as a potential ion exchange media for water softening and desalination.

In previous zeolite ion exchange studies, the most commonly used pre-treatment alkaline metal is Na^+; pre-treatment with NaCl has successfully increased zeolite's adsorption capacity for ammonium (Lei et al., 2008; Vassileva and Voikova, 2009) and heavy metals (Oliveira and Rubio, 2007; Xu et al., 2013). Pre-treating zeolite surfaces with Na^+ has also been proven successful at increasing the sorption capacity for cations associated with hard water (Ca^{2+} and Mg^{2+}), with results suggesting more complete exchange occurred as compared to natural zeolite (Chen et al., 2014; Bibiano-Cruz et al., 2016). Sodium has been extensively used for pre-treatment, based on the belief that it is easily exchangeable with specific cations of interest, increasing the adsorption

capacity. Previous studies have investigated the use of chloride salts, NaCl, $CaCl_2$ and KCl for the adsorption of heavy metals such as zinc, cadmium and nickel (Stefanović et al., 2007; Gedik and Imamoglu, 2008; Gorimbo et al., 2014). Previous studies have suggested limited success with KCl pre-treatment solutions, likely due to the highly selective preference for K^+ ions by clinoptilolite-rich zeolites (Cooney et al., 1999; Gedik and Imamoglu, 2008; Gorimbo et al., 2014); the use of KCl as a possible pre-treatment alternative was not investigated in this study. Honting Zhao and associates (2009) used a simulated hard water solution containing $CaCl_2$ and $MgCl_2$ (hardness of approximately 340 mg/L as $CaCO_3$) to successfully convert a locally available Na^+ –rich natural zeolite, thus allowing the zeolite to be used to remove Na^+ ions from coalbed natural gas co-produced waters (at concentrations of approximately 400 mg/L Na^+). This study expanded upon the concept introduced by Zhao, et al. 2009, by evaluating two local natural clinoptilolites, rich in Ca^{2+} and Na^+, for the dual treatment of water softening and desalination; however, focus was maintained on creating simulated natural conditions for both processes while characterizing the zeolite samples used. Cations in solution will exchange with cations on the zeolite framework based on selectivity; variation among published preference sequences suggest selectivity is influenced by clinoptilolite properties and will vary among samples. The basis of creating an integrated treatment process hinges on a near equivalent preference for Ca^{2+} and Na^+ ions. As salinity mitigation and water treatment are primary incentives, pre-treatment experiments were used in this study to both evaluate the effectiveness of NaCl and $CaCl_2$, as well as provide insight to the cation preferences for the zeolites studied.

The threat to water and soil quality from hard water (Ca^{2+}/Mg^{2+}) and sodium (Na^+) ions requires an economically viable and environmentally friendly remediation alternative. Another property leading to its use as an adsorbent is the ability of zeolite's exchange sites to hydrate and dehydrate cations reversibly; a zeolite used for ion exchange can be regenerated, which extends the cost effectiveness of zeolite (Li et al., 2008; Widiastuti et al., 2011). Regeneration of exchange sites will occur either when they are exposed to preferred cations, or cations of similar preference, at high solution concentrations. Previous studies have successfully evaluated using NaCl to regenerate Ca^{2+}/Mg^{2+}–zeolite (Tomić et al., 2012; Chen et al., 2014), at low hardness concentrations, and using Australian and Croatian zeolites. Synthetic hard water has also been used to regenerate Na^+–zeolite (Zhao et al., 2009); however, discussion of the results was quite limited. Regeneration studies involving saline and hard water samples is still quite limited and

significant variation among zeolite and solution samples exist. Majority of studies discussing regeneration of spent zeolite, are only focusing on the primary ion removal with the secondary cation solution serving only to regenerate the spent zeolite, essentially just reversing the reaction, with little attention taken to utilizing both stages effectively. This study expanded upon that theory by evaluating the reusability of the clinoptilolite through the creation of an integrated treatment process to treat two problem solutions. The inconsistent selectivity preference of clinoptilolite-rich zeolites for Na^+ and Ca^{2+} suggests that saline and hard water solutions could effectively create ion exchange treatment cycles and should effectively regenerate the spent zeolite at each stage.

The primary objective of this study was to create an integrated treatment process for desalination and water softening using zeolite ion exchange. This study focused on two natural clinoptilolite-rich zeolites obtained from North American mines and the acid treated counterpart of one of the zeolites; these zeolites were chosen based on preliminary research and the salinity mitigation experiments conducted in Chapter 2. The samples were characterized for important physiochemical properties for adsorption, such as CEC (exchangeable cations), surface area and chemical and mineral compositions. Batch adsorption experiments were conducted throughout this study to evaluate Na^+ sorption potential and total hardness reduction (Ca^{2+} and Mg^{2+} ions) of natural and acid treated zeolites. The zeolite samples (natural and acid treated) underwent pre-treatment batch tests with Na^+ and Ca^{2+}/Mg^{2+} ions to determine the most effective process, as well as suggested selectivity preferences of the zeolite samples. An integrated treatment process was designed based on the pre-treatment studies, with results outlining the regenerative capabilities of the zeolites, as well as their ability to be effective desalination and water softening systems.

3.3 Materials and Methodology

3.3.1 Material Characterization

Two natural zeolite samples were obtained from Bear River Zeolite Co. mine near Idaho, USA (BRZ) and the Canadian Zeolite Company's Bromley Creek mine in British Columbia, Canada (CMZ). To obtain consistency for particle size amongst samples, the natural zeolite was pulverized using a Bico UA disk pulveriser. Based on previous work, a sample of Bear River zeolite underwent acid treatment using 1.0M H_2SO_4 at an m/V ratio of 1g zeolite per 100mL acid solution and agitating the mixture for 30min. The zeolite received multiple washings with deionized water

(DI water) until a near neutral pH (7.05±0.35) of the wash solution was measured. The acid treated zeolite, BRZ(1M), was dried overnight (105°C) prior to manual disaggregation using a mortar and pestle until similar powdered consistency was achieved. The particle size distribution of BRZ, CMZ and BRZ(1M) was determined by the Malvern Mastersizer 2000.

The powdered zeolite samples were examined for mineralogical content by X-ray Diffraction (XRD) using Cu Kα radiation, 1.54Å (Bruker D4 Endeavor X-ray Diffractometer). An X-ray Fluorescence (XRF) Spectroscopy (Bruker S8 TIGER) instrument performed elemental analysis on the three zeolite samples. The specific surface area of each zeolite sample was measured by N_2 adsorption/desorption cycles performed with the Micromeritics ASAP2020 volumetric adsorption instrument (at 77K) and the Bruanauer-Emmett-Teller (BET) surface analysis process. A Scanning Electron Microscope (SEM) provided high magnification images of the zeolite framework using a variable pressure Hitachi S3000-N SEM apparatus.

The ability of zeolites to exchange cations, or the cation exchange capacity (CEC), was determined using an ammonium acetate method (pH=7) and conducted in triplicate for each sample (Hendershot et al., 2007). A 1M ammonium acetate (NH_4OAc) solution was used to extract exchangeable cations from the zeolite framework; the concentration of primary exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) was measured using inductively coupled plasma optical emission spectrometry (ICP-OES). The effective cation exchange capacity (ECEC) was calculated from the sum of the exchangeable cations (Hendershot et al., 2007; Ganjegunte et al., 2011) for BRZ and CMZ. An ion exchange reaction with the NH_4–zeolite and a 1M potassium chloride solution provided the CEC for BRZ(1M) through the analysis of the mass balance of K^+ ions (ICP-OES).

Standard stock solutions (Fisher Scientific Canada) of sodium (NaCl), calcium ($CaCl_2 \cdot 2H_2O$) and magnesium ($MgCl_2 \cdot 6H_2O$) were used to create synthetic saline and hard water solutions. This study aimed at simulating a practical integrated process with salinity reduction and water softening. To ensure relevance of the experiments, solutions were modelled with the same major ionic composition as the natural solutions; however, colloidal matter and other trace constituents found in the natural solutions were excluded.

The purpose of this study was to maintain a practical or natural relevance, thus, a small representation of ‘typical groundwater’ in the region was sampled. Groundwater was sampled from two rural wells located in central Saskatchewan, Canada, drilled at depths of approximately 5

metres (m) (Well A) and 7.5 m (Well B). Well A was sampled three times over a period of ten months to evaluate temporal influence while Well B was sampled once to introduce spatial variation. Synthetic hard water was used throughout the study to simulate the representative hardness, without the interference of other natural constituents. A synthetic hard water solution was created based on groundwater hardness data by dissolving analytical grade $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$ in DI water. It's been suggested that the carbonate content (calcite and dolomite mainly) accounts for the majority of this hardness; Saskatchewan's carbonate content has been found to be above 50% of soil constituents, with higher ratios of calcite to dolomite (Rostad and Arnaud, 1970). It is common for calcium to contribute more to the total hardness than magnesium, thus, a synthetic hard groundwater solution was created with calcium ions contributing 60% while magnesium ions accounted for 40%. The total hardness was measured using a photometric titration device (Mettler Toledo T50 with Phototrode DP5 for hardness determination). Samples were prepared for titration by diluting to 50 mL prior to adding 1-2 mL of a pH buffer (magnesium salt of EDTA) solution to obtain a pH of 10.0-10.1 and dissolving 0.2g of Eriochrome (E512-25) Black T indicator (Betz and Noll, 1950; ASTM, 2012). A 0.01M EDTA titrant solution (Ethylenediamine Tetraacetic acid, Disodium salt dehydrate certified ACS crystalline) was added at automatic intervals, with continuous stirring, until the end-point color change (violet to blue) was detected by the phototrode. The procedure and instrument set up followed Mettler Toledo Titration Application for total hardness (M405-2009). The photometric titration device provided breakthrough curves, volume of titrant added and calculated total hardness (mg/L as $CaCO_3$). The pH was measured using a Hach HQ40d multi meter (PHC28101).

To simulate potential practical applications, batch equilibrium adsorption experiments were conducted to determine the maximum adsorption capacities for sodium. Batch adsorption experiments were conducted in triplicate by mixing 5.0 g of powdered zeolite with 30mL of synthetic Na^+ solution (250−10,000 mg/L), creating a m/V ratio of 0.17. Ion exchange occurred at room temperature (approximately 23°C), over a 24 hour period with continuous agitation by a reciprocal shaker (New Brunswick Scientific Co. Laboratory Rotator – G2). The suspension was separated into solid and liquid phases using a centrifuge (Eppendorf 5804R-15 amp) operating at 200 rpm. The liquid was decanted and the sorption solution analyzed with a sodium ion selective electrode (Thermoscientific ROSS Sodium Ion Sensitive Electrode and Orion Star A214 Benchtop Meter). The Na^+ solution was created by dissolving analytical grade NaCl in DI water. The sodium

selective electrode, photometric titration device and ICP-OES generated cation concentrations in milligrams per litre (mg/L). With the exception of the sorption isotherms, the data in this study presented the concentration of cations using milliequivalents per litre (meq/L). The equivalent weight of an ion is the molecular weight divided by the valence charge and it was used to convert the ion concentrations from mg to meq.

3.3.2 Integrated Treatment Process

This study included two complete ion exchange stages using synthetic sodium and hard water solutions, as visually presented in Figure 3.1.

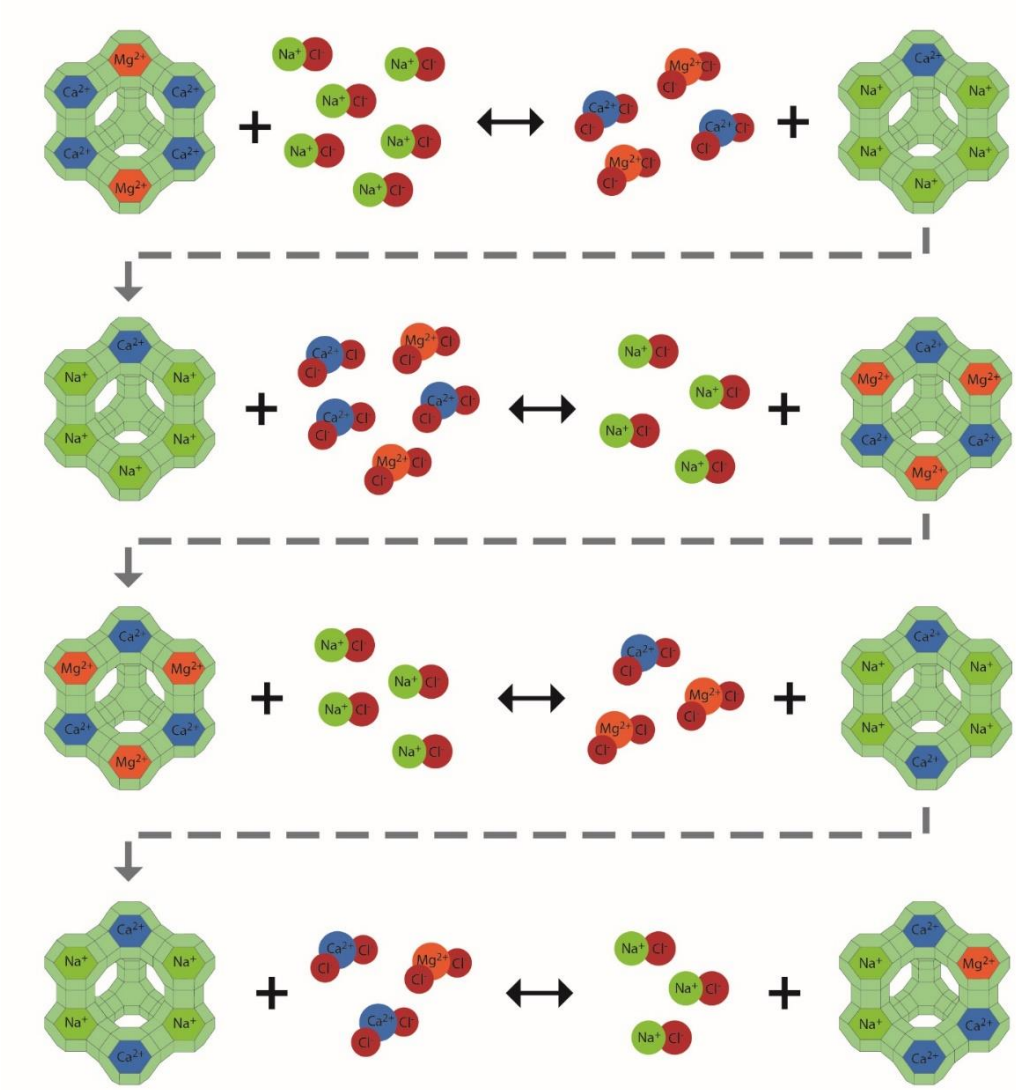


Figure 3.1: Graphical representation of the sodium removal and hard water treatment process.

The concentration of Na^+ and Ca^{2+}/Mg^{2+} ions in respective synthetic solutions were chosen based on preliminary groundwater analysis and sodium batch equilibrium adsorption experiments for each zeolite. Previous research found it beneficial to pre-treat the zeolite with ions that are easier to remove during ion exchange; the primary exchangeable cations (Na^+, Ca^{2+}, Mg^{2+} and K^+) are exchanged for a singular cation to create homoionic conditions on the zeolite surface; however, K^+ is typically removed to a lesser degree due to selective preference for the cation by zeolite (Mumpton, 1999; Liu and Lo, 2001). Studies have predominately used NaCl to pre-treat the zeolite, anticipating easier removal of ions from solution when exchanging with Na^+.

$$[NaCl] + \begin{bmatrix} Ca^{2+} \\ K^+ \\ Mg^{2+} \end{bmatrix} - Zeolite \leftrightarrow \begin{bmatrix} CaCl_2 \\ KCl \\ MgCl_2 \end{bmatrix} + [2Na^+] - Zeolite \quad (3.1)$$

Clinoptilolite-rich zeolites for sodium mitigation have been pre-treated or regenerated with $CaCl_2$, with studies finding increased Na^+ adsorption capacity as a result (Zhao et al., 2009).

$$[CaCl_2] + \begin{bmatrix} Na^+ \\ K^+ \\ Mg^{2+} \end{bmatrix} - Zeolite \leftrightarrow \begin{bmatrix} NaCl \\ KCl \\ MgCl_2 \end{bmatrix} + [Ca^{2+}] - Zeolite \quad (3.2)$$

Creating an integrated treatment process for both Na^+ mitigation and water softening was the principle objective of this study; therefore, it was important to evaluate the pre-treatment of the zeolite in terms of NaCl and $CaCl_2/MgCl_2$. Pre-treatment, batch adsorption experiments were conducted on BRZ, CMZ and BRZ(1M) to determine the optimum ion exchange order for this study. Batch adsorption experiments were performed with the previously mentioned experimental parameters including contact time (24 hour), m/V ratio (0.17), temperature (23°C) and agitation (200 rpm). The respective sorption solutions were measured using the automated EDTA titration device and sodium sensitive electrode. The chemical analysis for the regeneration potential was supported with XRF analysis, as well as SEM images.

Based on the optimum pre-treatment solution chosen in this study, an integrated treatment process was designed to create ion exchange cycles for sodium uptake and hard water treatment. A single cycle contains two individual adsorption stages representing water softening (Ca^{2+}/Mg^{2+}) and Na^{+} removal; each ion exchange cycle can be described by the following chemical formulas:

$$\text{Stage 1:} \quad CaCl_2(or\ MgCl_2) + Zeolite \leftrightarrow NaCl + Ca/Mg - Zeolite \tag{3.3}$$

$$\text{Stage 2:} \quad NaCl + Ca/Mg - Zeolite \leftrightarrow CaCl_2(or\ MgCl_2) + Na - Zeolite \tag{3.4}$$

Batch adsorption experiments yielded sorption solutions at each stage which were analyzed for respective cation concentration adsorbed (EDTA titration and sodium selective electrode) and resulting pH.

3.3.3 Statistical Analysis

Batch equilibrium adsorption experiments were performed in triplicate for each sample, throughout the entire study. Statistical analysis was performed on the data with GraphPad Prism 6.0 software. Data comparisons were primarily completed using the one- and two-way analysis of variance (ANOVA). Pair-wise comparisons were primarily calculated using the post-hoc Bonferroni and Dunnett tests. A significance level of $p \leq 0.05$ (95% confidence interval) was used for all comparisons. The symbols representing significance in the figures corresponds to the following p-values: $p \leq 0.05$ (*), $p \leq 0.01$ (**), $p \leq 0.001$ (***), and $p \leq 0.0001$ (****) with no asterisk meaning the hypothesis is not statistically significant ($p > 0.05$).

3.4 Results

3.4.1 Material Characterization

The zeolite samples were pulverized to powder as it has been suggested that smaller zeolite particle sizes have larger surface areas and shorter pathways for diffusion (Cui et al., 2006), thus, increasing the maximum adsorption capacity (Pansini, 1996; Vivacqua et al., 2013). The particle size distribution for the zeolite samples is presented in the supplementary data (Figure 3.9), with the resulting BET-N_2 surface areas presented in Table 3.1.

Table 3.1: Physiochemical properties of natural (BRZ and CMZ) and acid treated (BRZ(1M)) zeolites. Values represent the mean results and standard deviation.

		BRZ	CMZ	BRZ(1M)
CEC (meq/100g)		138.4 ± 5.5 [1]	100.5 ± 4.6 [1]	158.7 ± 6.8
Exchangeable Ions (meq/100g)	Na^+	18.6 ± 0.1	33.2 ± 0.5	—
	Ca^{2+}	66.5 ± 0.1	29.5 ± 1.1	—
	Mg^{2+}	3.4 ± 0.1	1.8 ± 0.1	—
	K^+	41.6 ± 1.2	39.2 ± 0.4	—
% Clinoptilolite		85.6	69.3	86.1
Si/Al Ratio		6.2	5.5	6.8
BET-N_2 (m^2/g)		37	32	66

[1] – Effective cation exchange capacity (ECEC)

The BET-N_2 surface areas were measured to be 37, 32 and 66 m^2/g for BRZ, CMZ and BRZ(1M) respectively. The surface area increased as a result of 1M H_2SO_4 treatment, as suggested in previous studies (Li et al., 2011; Wang et al., 2012), was likely due to the formation of more channels, cracks and micropores resulting in an enlarged pore system (Liu and Yan, 2000; Jozefaciuk, 2002).

Each zeolite studied was characterized based on mineralogical content, particle size, chemical composition and exchangeable cations (cation exchange capacity). XRD analysis suggests BRZ, CMZ and BRZ(1M) are primarily clinoptilolite-rich zeolites with compositions of 85.6%, 69.3%, and 86.1% respectively (individual component results are presented in Table 3.7 in the supplementary data). Clinoptilolite-rich zeolites often contain other silicate minerals which are commonly referred to as impurities due to potential negative impacts they can have on the zeolite's sorption potential (Curkovic et al., 1996; Yukselen-Aksoy, 2010). All of the zeolites studied contained varying compositions of quartz, cristobalite and illite. Quartz group minerals (quartz and cristobalite) are inactive for ion exchange due to the inexistence of aluminum atoms on the three-dimensional framework, thus, yielding a neutral surface charge (Inglezakis, 2005). Illite are analogous to clinoptilolite, as it has a negative surface charge allowing for substitution of exchangeable cations (Inglezakis, 2005). As anticipated due to previous studies (Li et al., 2008; Wang et al., 2012; Rivera et al., 2013), zeolite acid-modification did not appear to significantly alter the zeolite's mineralogical composition.

The zeolite's Si/Al ratios were calculated from chemical compositions (weight/weight %) of SiO_2 and Al_2O_3 obtained from XRF analysis (Table 3.8 in the supplementary data); the Si/Al ratios for BRZ, CMZ and BRZ(1M) were 6.2, 5.5 and 6.8 respectively, which are slightly higher than anticipated (4.0-5.5) (Erdem et al., 2004; Inglezakis et al., 2004). Acid treatment has been reported to cause dealumination or the leaching of aluminum ions out of the framework due to Al–O bonds breaking (Xu et al., 2014). The slight increase in Si/Al ratio for BRZ(1M) could be explained by the occurrence of dealumination (Haldun Kurama et al., 2002; Cheng et al., 2005).

The cation exchange capacity is the measure of cations adsorbed in exchange for those cations naturally present on the negatively charged sites of the zeolites (Inglezakis et al., 2004; Carter and Gregorich, 2008). The CEC and primary exchangeable cations are listed in Table 3.1 for BRZ, CMZ and BRZ(1M). The effective CEC of BRZ is approximately 138 meq/100g, based on an ammonium exchange method; the primary exchangeable cations, in order of abundance, are Ca^{2+} > K^+ > Na^+ > Mg^{2+}. CMZ's exchangeable cations naturally occur as K^+ > Na^+ > Ca^{2+} > Mg^{2+}; the summation of exchangeable cations resulted in an effective CEC of approximately 101 meq/100g. The CEC of BRZ(1M) is approximately 159meq/100g; the increased CEC for BRZ(1M) (compared to BRZ), suggests that the acid treated zeolite should have more sites available for ion exchange. Acid treatment altered the exchangeable cations present on the zeolite surface, generating protonic adsorption sites which has been suggested to increase the zeolite's sorption capacity (Salvestrini et al., 2010; Rivera et al., 2013; Santiago et al., 2016). The chemical pre-treatment applied to BRZ(1M) suggests homoionic sites, thus eliminating the need of exchangeable cation determination.

The hardness of groundwater was measured temporally and spatially to demonstrate the occurrence of natural variation. Well A was sampled three times over a period of ten months to evaluate temporal influence while Well B was sampled once to add spatial variation (Table 3.2). A synthetic Ca^{2+}/Mg^{2+} solution with a total hardness of approximately 15 meq/L (750 mg/L) as $CaCO_3$ was determined appropriate for this study. The solution consisted of dissolving 0.705g $CaCl_2 \cdot 2H_2O$ and 0.650g $MgCl_2 \cdot 6H_2O$ in 1L of DI water. The total hardness was measured, using a photometric titration device, to be 15.3 ± 0.2 meq/L as $CaCO_3$.

Table 3.2: The total hardness measured by EDTA titration for groundwater samples from two rural wells in Saskatchewan, Canada. Well locations are separated by approximately 10 kilometres with a maximum depth of approximately 7 m.

		September 2015	April 2016		July 2016
		Well A	Well A	Well B	Well A
Total Hardness	mg/L as $CaCO_3$	513	431	793	623
	meq/L as $CaCO_3$	10.2	8.6	15.9	12.5

Adsorption isotherms describe mathematical relationships between the concentration of a particular ion adsorbed to a solid media and that remaining in solution (Foo and Hameed, 2010). Adsorption equilibrium isotherms played a critical role in designing an effective adsorption system. The graphical representation expresses the mass of ions adsorbed on the solid phase (q) and the equilibrium concentration of the particular ion in solution (C). The following equation was used to determine q (mg/g), where C_0 and C_e (mg/L) are respectively, the concentration of Na^+ in the solution initially and at equilibrium, V (L) is the volume of Na^+ solution used and m is the mass of zeolite (g) (Ghaly and Verma, 2008).

$$q = \frac{V \times (C_e - C_0)}{m} \tag{3.5}$$

The Langmuir model is based on the concept of monolayer adsorption (Foo and Hameed, 2010) and that adsorption can only occur at a finite number of sites (Fetter, 1993). The Langmuir equation is often used to determine q_e which is the maximum adsorption capacity of the zeolite (mg/g) and K_L, which is the coefficient related to the affinity of the solute and adsorbent (Volesky, 2003).

$$q = \frac{q_e K_L C_e}{1 + K_L C_e} \tag{3.6}$$

The Langmuir and Freundlich isotherm models were applied based on the non-linear squares method to analyze adsorption potential and isotherm fit. The Freundlich model assumes multilayer adsorption on heterogeneous adsorption sites where K_F [(mg/g)(L/mg)$^{1/n}$] is the Freundlich constant and n is the dimensionless Freundlich exponent (Fetter, 1993).

$$q = K_F C_e^{1/n} \tag{3.7}$$

The non-linear squares method uses the Araike's Information Criterion (AIC) to assess the fit of the isotherm models (El-Khaiary and Malash, 2011).

$$AIC = Nln\frac{SSE}{N} + 2N_P + \frac{2N_P(N_P+1)}{N-N_P-1} \tag{3.8}$$

where *N* refers to the number of data points, SSE is the sum of squared deviations of the points from the regression curve and N_P is the number or parameters in the associated models. The evidence ratio was used to compare the AIC values of the two models, where *ΔAIC* is the absolute value of the difference in AIC between the Langmuir and Freundlich models:

$$Evidence\ Ratio = e^{0.5(\Delta AIC)} \tag{3.9}$$

Figure 3.2 modeled the experimental data for BRZ, CMZ and BRZ(1M) using the Langmuir isotherm model whereas Table 3.3 presents the non-linear squares parameters evaluating the fit of the Langmuir and Freundlich models to the data.

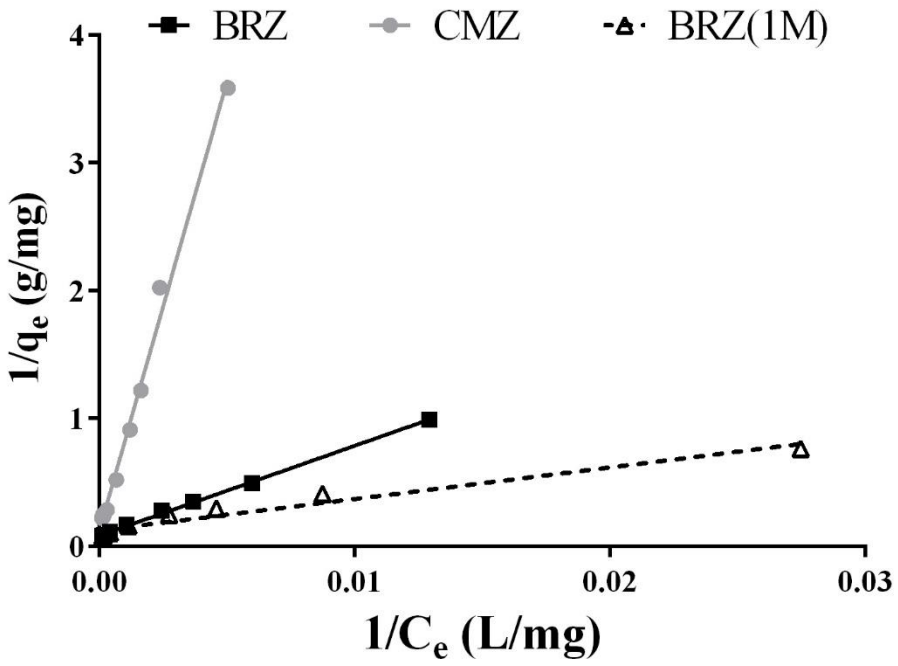


Figure 3.2: Langmuir isotherm analysis for BRZ, CMZ and BRZ(1M) to evaluate sodium saturation. Batch adsorption experiments conducted over an initial Na^+ concentration range of 250 to 10,000 mg/L (10.9 to 435 meq/L) at m/V ratio of 0.17.

Table 3.3: Isotherm model parameters from the non-linear squares analysis for batch adsorption experiments conducted on BRZ, CMZ and BRZ(1M) at a mass to volume ratio of 0.17. The average pH for the initial Na^+ solution range (250-10,000mg/L) was 6.01 ± 0.42.

Model	Parameters	BRZ	CMZ	BRZ(1M)
Langmuir	q_e (mg/g)	13.9 ± 0.3	6.3 ± 0.5	13.1 ± 0.6
	K_L	0.0008 ± 0.00006	0.0003 ± 0.00006	0.0012 ± 0.00021
	R^2	0.997	0.984	0.980
	Sy.x	0.28	0.24	0.66
Freundlich	K_F [(mg/g)(L/mg)$^{1/n}$]	0.31 ± 0.09	0.03 ± 0.02	0.50 ± 0.08
	n	2.4 ± 0.2	1.8 ± 0.2	2.7 ± 0.1
	R^2	0.975	0.946	0.989
	Sy.x	0.76	0.43	0.50
Δ AIC		-17.64	-10.96	5.07
Evidence Ratio		6,759	270	12.6
Preferred Model		Langmuir	Langmuir	Freundlich
Average Sorption Solution pH		6.96 ± 0.09	5.84 ± 0.04	2.26 ± 0.31

± – corresponds to the standard error

The Langmuir model sufficiently described monolayer Na^+ adsorption for BRZ and CMZ, as confirmed by evidence ratios of 6,759 and 240 for BRZ and CMZ respectively. For the acid treated zeolite, BRZ(1M), Na^+ uptake tended to be more linear, therefore, the Freundlich model provided a better fit than the Langmuir model, as supported by a coefficient of correlation (R^2) of 0.989. The maximum adsorption capacity for Na^+, q_e, suggests the Na^+ saturation point for each zeolite. The maximum adsorption capacity for Na^+ uptake was 13.9 ± 0.3 and 6.3 ± 0.5 mg/g for BRZ and CMZ respectively. The pH response suggests that Na^+ sorption with BRZ increases slightly while the pH of CMZ's sorption solution showed an insignificant decrease from the original Na^+ solution. Adsorption experiments conducted using BRZ(1M) resulted in an acidic sorption solution, which would be problematic in practice. Based on the batch adsorption results and a desire to simulate practical application, a synthetic sodium solution was created by diluting analytical grade NaCl in DI water, obtaining a Na^+ concentration of 544 ± 8 meq/L; the initial Na^+ concentration was measured by diluting the solution prior to Na^+ measurement with the sodium selective electrode.

3.4.2 Pre-Treating Zeolite Adsorbents

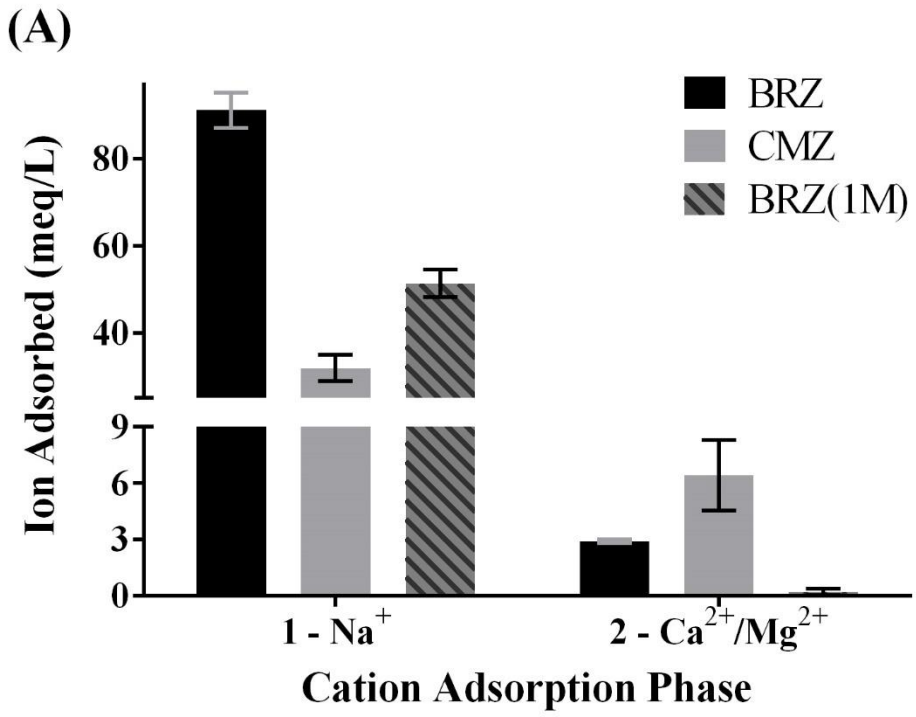
Pre-treating zeolite with an exchangeable cation that is believed to be more easily removed, has proven to improve the ion exchange capacity. The influence of pre-treating with both hard water and sodium solutions were evaluated. The adsorbed concentrations were determined using a mass balance equation, utilizing the solution's initial and final cation concentrations. The initial concentrations used throughout the pre-treatment experiments were 544 ± 8 meq/L Na^+ and a total hardness of 15.3 ± 0.2 meq/L as $CaCO_3$ with pH values of 6.1 ± 0.4 and 5.9 ± 0.3 respectively. The adsorbed concentration of Na^+ was calculated from measurements of the initial and final (sorption) concentrations using the sodium sensitive electrode. The total hardness, or Ca^{2+}/Mg^{2+} cations, adsorbed was measured using an EDTA auto-titration device to determine the total hardness of the initial and ion exchange sorption solutions.

$$Na^+_{Adsorbed} = Na^+_{Initial\ Sol.} - Na^+_{Sorption\ Sol.} \tag{3.10}$$

$$T.Hardness_{\ Adsorbed} = T.H_{\ Intitial\ Sol.} - T.H_{\ Sorption\ Sol.} \tag{3.11}$$

Previous studies have commonly used NaCl to create homoionic Na^+ exchange sites (Cooney et al., 1999; Panayotova, 2001). As shown in Figure 3.3 (A), the zeolite samples were pre-treated initially with Na^+ ions prior to being used as an ion exchange media for hard water ions, Ca^{2+} and

Mg^{2+}. BRZ, CMZ and BRZ(1M) adsorbed 91.1, 31.9 and 51.3 meq/L of Na^{+} respectively. BRZ was able to adsorb significantly more Na^{+} ions than the other two zeolites based on a Bonferroni post-hoc test and significance level of 0.05. The Na^{+} pre-treated zeolite, underwent batch adsorption experiments with synthetic hard water to evaluate the exchange potential with Ca^{2+} and Mg^{2+} ions. The total hardness reduction from adsorption by BRZ, CMZ and BRZ(1M) was 2.9, 6.4 and 0.2 meq/L respectively. The pH of the sorption solutions was measured after pre-treatment and hard water adsorption, as shown in Figure 3.3 (B), for BRZ, CMZ and BRZ(1M); a Dunnett post-hoc multiple comparison analysis was conducted, comparing the pH response to sorption with the initial solution pH. The pH response for BRZ sorption experiments increased after pre-treatment with the NaCl and ion exchange with the hard water solution. Ion exchange with the pre-treatment Na^{+} solution resulted in a slight decrease ($p \leq 0.05$) in pH and an insignificant ($p > 0.05$) change with Ca^{2+}/Mg^{2+} sorption. The pH response of the solution after sorption experiments with BRZ(1M) decreased significantly ($p \leq 0.0001$) for both Na^{+} and hard water solutions with pH values of approximately 1.83 and 2.65 respectively. The pH response from BRZ(1M) ion exchange experiments was very acidic and the adsorption potential for Ca^{2+}/Mg^{2+} after pre-treatment was poor, therefore, the acid treated zeolite, BRZ(1M), was eliminated as a possible adsorbent for an integrated treatment process.



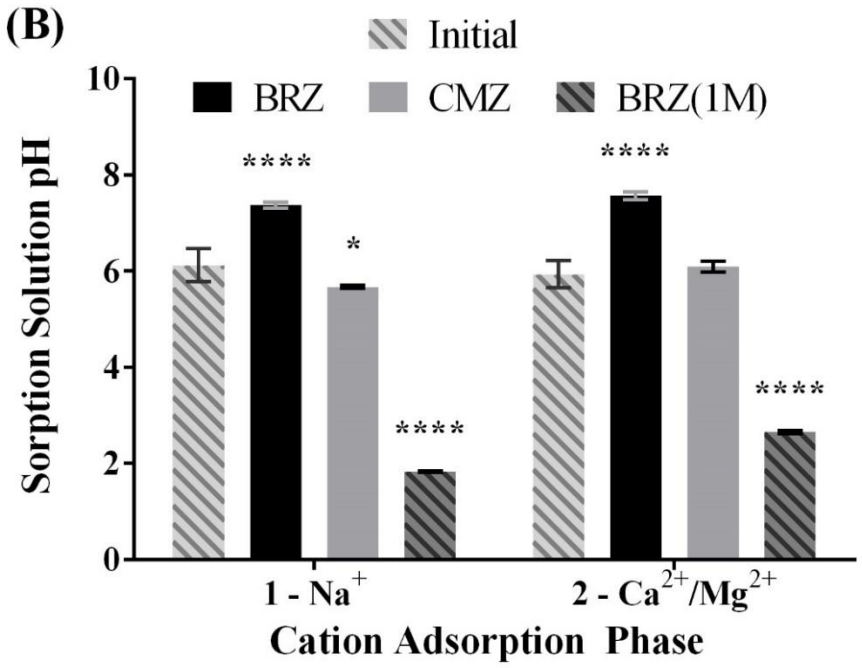


Figure 3.3: Hard water treatment using a pre-treated, homoionic, Na^+–zeolite (A). The pH response from the batch adsorption process (m/V ratio of 0.17) compared to initial solution pH (B). Values represent the mean results and standard deviation.

Pre-treating zeolite with $CaCl_2$ to create Ca^{2+} exchange sites is less common in previous literature. A Ca^{2+} and Mg^{2+} cation solution, with a total hardness of 15.3 ± 0.2 meq/L as $CaCO_3$, introduced these cations to the natural zeolite samples through a batch adsorption pre-treatment technique. The pre-treated zeolite was directly used for Na^+ removal from a simulated saline solution with a Na^+ concentration of 544 ± 8 meq/L Na^+. The total hardness (Ca^{2+} and Mg^{2+} ions) adsorbed for pre-treatment and the Na^+ ions adsorbed during the second adsorption stage, are shown in Figure 3.4 (A) for BRZ and CMZ. Pre-treatment of CMZ was significantly ($p \leq 0.0001$) more successful than BRZ, with the total hardness adsorbed measured at 1.2 and 10.1 meq/L respectively. However, the difference in Na^+ ion adsorbed during the second stage was insignificant ($p > 0.05$); BRZ adsorbed 145 meq/L Na^+ while CMZ adsorbed 139 meq/L. Statistical analysis was completed using two-way ANOVA and the Bonferroni post-hoc multiple comparison test. The pH response in comparison to the initial solution pH for each adsorption stage is shown in Figure 3.4 (B). Adsorption with BRZ during pre-treatment with the hard water solution increased the pH ($p \leq 0.0001$) while the solution pH insignificantly changed as a result of adsorption with natural

CMZ and the hard water. The pH of the Na^+ solution also increased after exposure to the pre-treated or Ca^{2+}/Mg^{2+}–BRZ ($p \leq 0.0001$); however, exposure to the Ca^{2+}/Mg^{2+}–CMZ resulted in a slight decrease ($p \leq 0.05$) of the Na^+ sorption solution pH. Statistical analysis of the pH response to the adsorption stages was completed using two-way ANOVA and the Dunnett test to compare the effects against the control or initial pH.

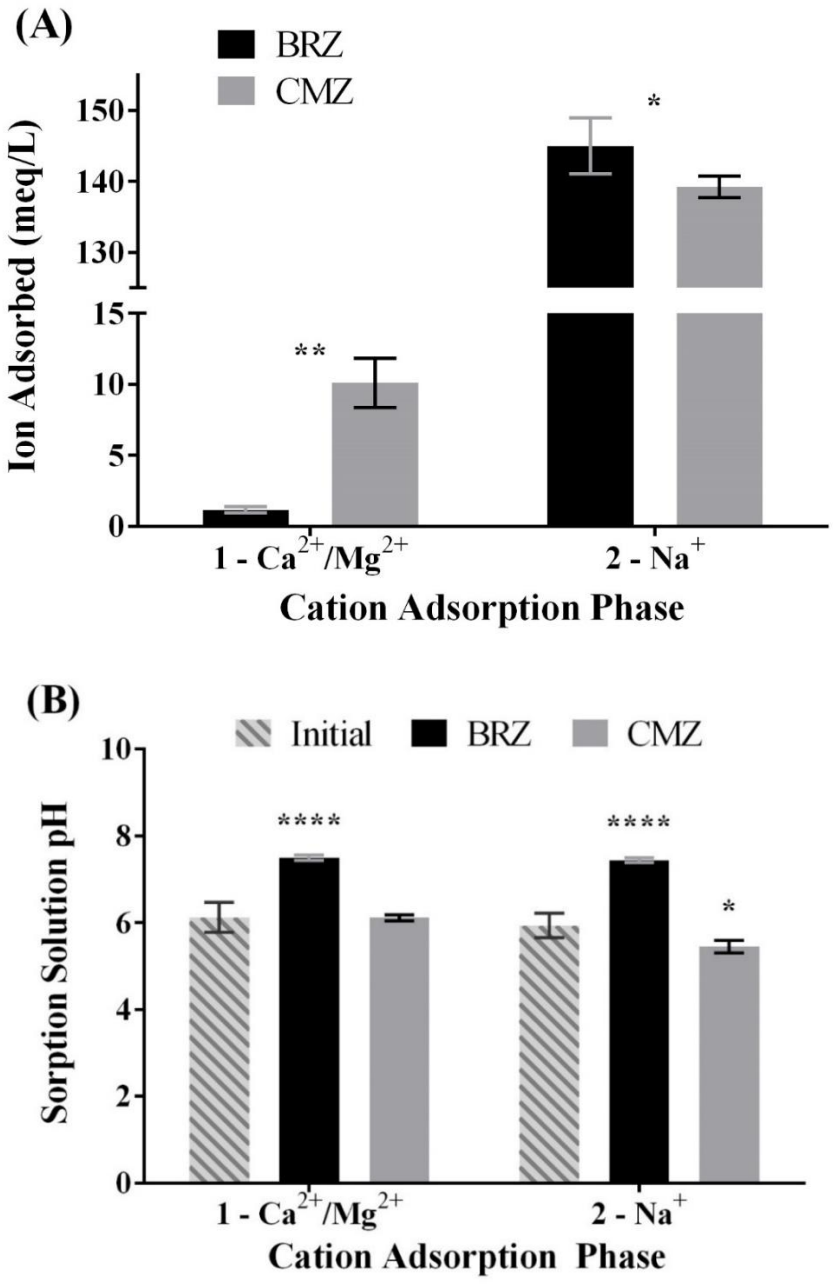


Figure 3.4: Zeolite treated with Ca^{2+} and Mg^{2+} ions, prior to its use for Na^+ removal (A) with the corresponding pH response (B). Adsorption experiments conducted using synthetic solutions with an m/V ratio of 0.17. Values represent the mean results and standard deviation.

Table 3.4 contains the adsorbed concentrations of Na^+ and Ca^{2+}/Mg^{2+} ions at each stage, for both pre-treatment cation evaluations. Pre-treatment with Na^+ ions successfully increased the adsorption of the hardness ions (Ca^{2+}/Mg^{2+}) for BRZ by nearly 150% compared to hardness adsorption by natural BRZ. The adsorbed concentration of hardness ions decreased with the Na^+–CMZ adsorbent, by approximately 36%, in comparison to adsorption with natural CMZ. Pre-treatment with a hard water solution composed of Ca^{2+} and Mg^{2+} ions, successfully increased the removal of Na^+ ions in comparison to the natural forms of BRZ and CMZ. The adsorption of Na^+ ions by Ca^{2+}/Mg^{2+}–BRZ and Ca^{2+}/Mg^{2+}–CMZ increased by approximately 59% and 336% respectively, when compared to Na^+ adsorption by natural BRZ and CMZ. Graphical and statistical representation of the data presented in Table 3.4 is shown in the supplementary data (Figure 3.10).

Table 3.4: Adsorbed cation concentrations from pre-treatment ion exchange experiments with BRZ and CMZ. Values represent the mean results and standard deviation.

		Na^+ (meq/L)	Total Hardness (Ca^{2+}/Mg^{2+}) (meq/L as $CaCO_3$)
Initial Concentration		544 ± 8	15.3 ± 0.2
1–Na^+ → 2–Ca^{2+}/Mg^{2+}	BRZ	91.1	2.9
	CMZ	31.9	6.4
1–Ca^{2+}/Mg^{2+} → 2–Na^+	BRZ	145	1.2
	CMZ	139	10.1

3.4.3 Integrated Treatment Process

Based on the previously suggested regeneration potential of CMZ and BRZ (Table 3.4), an integrated treatment process was designed (Figure 3.1) to include cycles with hard-water softening (Ca^{2+}/Mg^{2+}) as the first sorption stage and salinity mitigation (Na^+) as the second. Five complete regeneration cycles were carried out, recycling the cation-spent zeolite for each batch adsorption stage. The initial hard water and Na^+ concentrations and pH values for the solutions used during the dual treatment cycles is presented in Table 3.5.

Table 3.5: The initial concentrations and pH values for the Ca^{2+}/Mg^{2+} and Na^{+} synthetic solutions used for the integrated treatment process. Values represent the mean and standard deviation.

Solution	Concentration (meq/L)	pH
Ca^{2+}/Mg^{2+}	15.3 ± 0.2	5.9 ± 0.3
Na^{+}	544 ± 8	6.1 ± 0.4

The concentration adsorbed during exchange was determined using the concentration remaining in solution and a mass balance approach for each adsorption stage. The concentration of Ca^{2+}/Mg^{2+} ions depicted in Figure 3.5 correlates to the total hardness reduction measured in the sorption solutions, whereas the Na^{+} stages directly shows the adsorbed Na^{+} concentration.

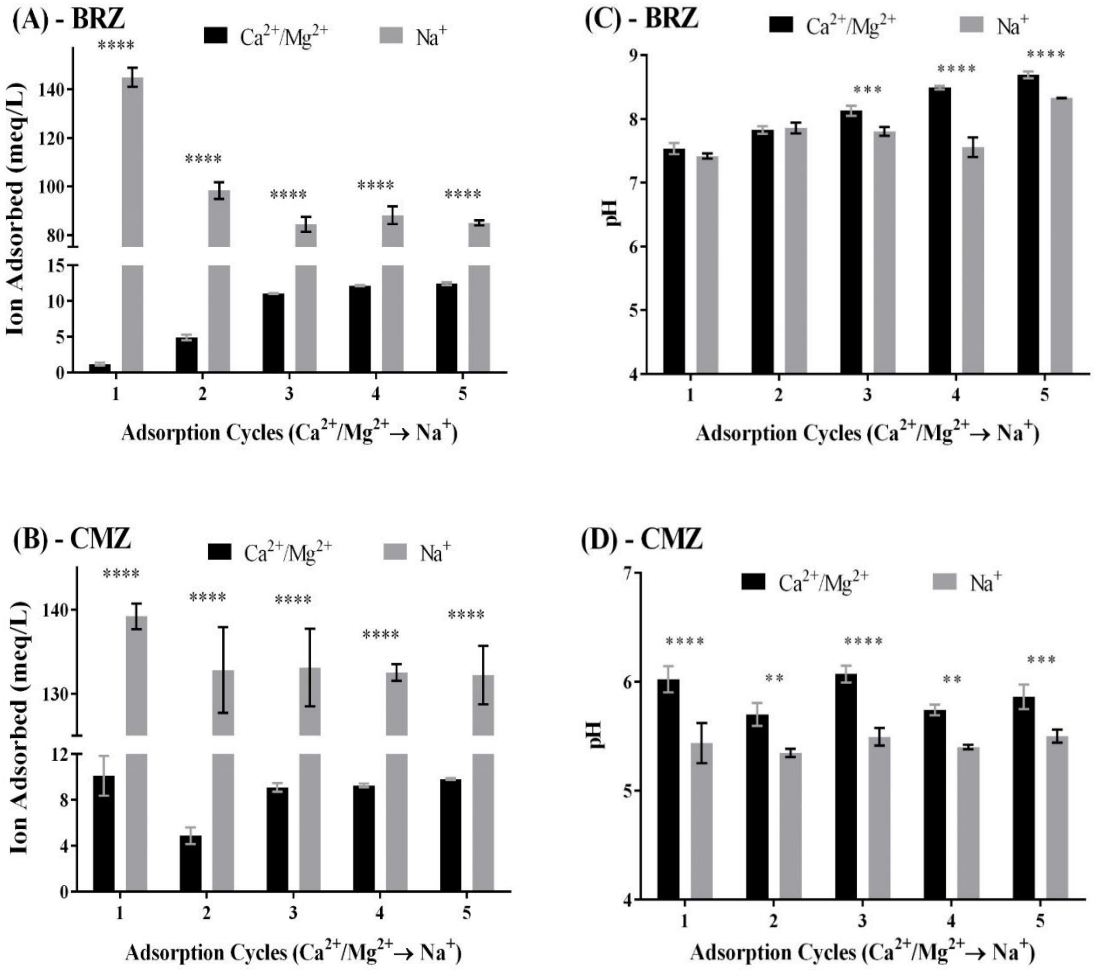


Figure 3.5: Integrated treatment process for water softening and Na^{+} uptake for BRZ (A) and CMZ (B) using an m/V ratio of 0.17. The pH response of sorption solutions for BRZ (C) and CMZ (D) throughout the regeneration cycles. Values represent the mean results and standard deviation.

The integrated treatment process with BRZ (Figure 3.5 (A)) shows that the adsorbed Na^+ concentration is highest during the first Na^+ sorption stage, whereas the concentration of adsorbed total hardness cations increased with successive cycles. A less drastic decrease in Na^+ concentration is seen for CMZ (Figure 3.5 (B)) after the initial cycle and it is unclear why the hardness reduction dipped during the second cycle. Water softening and Na^+ uptake during the last three complete cycles (3 to 5) appears to have created a stable functioning adsorption system; the difference in the adsorbed concentration is insignificant ($p>0.05$) for Ca^{2+}/Mg^{2+} and Na^+ for CMZ (ordinary one-way ANOVA using Tukey multiple comparisons with single pooled variance). BRZ's pH response to regenerative adsorption cycles was insignificant until the third cycle where hard water sorption solutions increased the pH while Na^+ sorption caused it to decrease. The pH of both sorption solutions significantly ($p\leq0.0001$) increased in comparison to the initial pH values of 5.93 and 6.12 for Ca^{2+}/Mg^{2+} and Na^+ respectively. The sorption solutions from CMZ's integrated process was cyclical, with the pH increasing with the Ca^{2+}/Mg^{2+} sorption solution and decreasing for Na^+; the variation from the initial synthetic solution was mainly insignificant ($p>0.05$).

The regeneration potential of zeolite associated with the integrated treatment process was determined by comparably measuring the ion concentration removed during each adsorption stage with the cation uptake occurring during adsorption with natural zeolite. A direct comparison of the ability of regenerated zeolite (Na^+–zeolite) to remove hardness cations (Ca^{2+}/Mg^{2+}) is shown in Figure 3.6 for BRZ (A) and CMZ (B). The Na^+–BRZ forms increased total hardness reduction over the natural BRZ form ($p\leq0.0001$); however, the Ca^{2+}/Mg^{2+} adsorption was significantly less during the third ($p\leq0.01$) and fifth ($p\leq0.001$) adsorption stages compared to the seventh and ninth, which are insignificantly different ($p>0.05$). The removal of hardness cations by regenerated Na^+–CMZ was lowest during the third stage (second complete cycle) ($p\leq0.0001$), before increasing during successive cycles. There was an insignificant difference ($p>0.05$) in adsorbed Ca^{2+}/Mg^{2+} concentration between the natural CMZ and the fifth, seventh and ninth stages, as well as individually between those stages. The increase in adsorbed Ca^{2+}/Mg^{2+} concentration for BRZ and essentially unchanged hardness reduction for CMZ during successive stages suggests Na^+ suitability for regeneration.

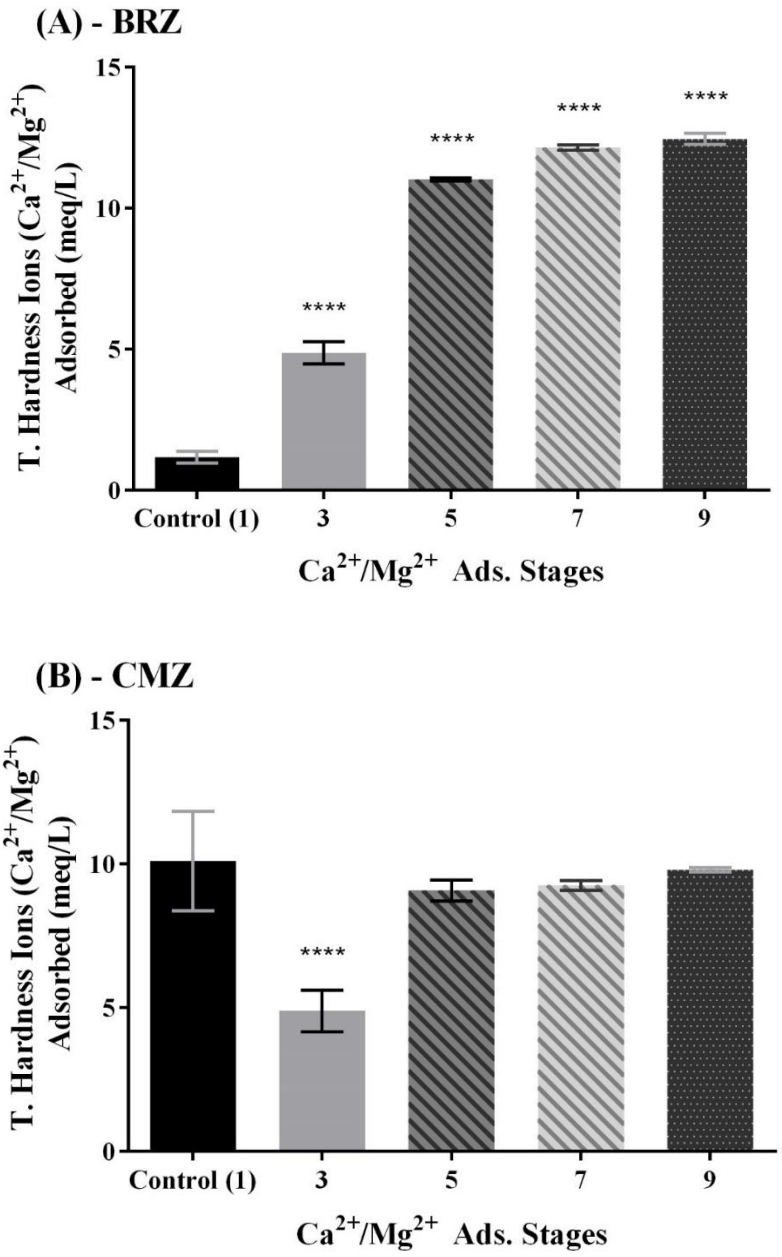
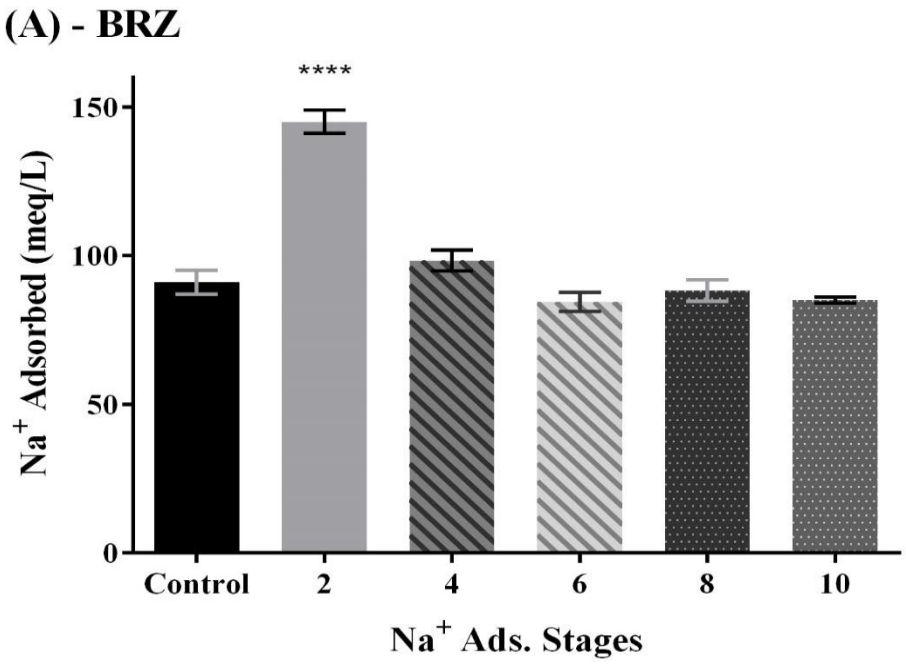


Figure 3.6: Evaluating the influence of using regenerated zeolites (Na^+–zeolite), BRZ (A) and CMZ (B), on total hardness reduction. Values represent the mean results and standard deviation. The total hardness of the initial synthetic solution was 15.3 ± 0.2 meq/L as $CaCO_3$.

The Na^+ uptake stages shown in Figure 3.7 used natural zeolite (control) and Ca^{2+}/Mg^{2+} pre-treated and regenerated BRZ (A) and CMZ (B) adsorbents. The Na^+ uptake with Ca^{2+}/Mg^{2+}–BRZ increased during the second adsorption stage (first cycle), obtaining the highest Na^+ removal among adsorbents. The concentration of Na^+ ion adsorbed then reduced to a near consistent

adsorbed Na^+ concentration during successive stages; the Na^+ uptake by Ca^{2+}/Mg^{2+}–BRZ during the sixth, eighth and tenth stages varied insignificantly ($p>0.05$) in comparison to each other and the natural zeolite (control). The Na^+ concentration removed during the fourth adsorption stage (second cycle) was significantly different than the second stage ($p\leq0.0001$) as well as the sixth, eighth and tenth Ca^{2+}/Mg^{2+}–BRZ stages ($p\leq0.01$). As seen in Figure 3.7 (A), the pre-treatment or regeneration with Ca^{2+}/Mg^{2+} ions, increased the Na^+ uptake significantly over the natural CMZ. The concentration of Na^+ ions adsorbed by Ca^{2+}/Mg^{2+}–CMZ was highest during the second adsorption stage; however, the Na^+ removal during successive cycles was statistically insignificant ($p>0.05$). Statistical analysis was performed using ordinary one-way ANOVA as well as post-hoc multiple comparisons tests among cycles (Bonferroni) and against the control samples (Dunnett), using single pooled variances. The Dunnett analysis is represented on Figure 3.6 and Figure 3.7.



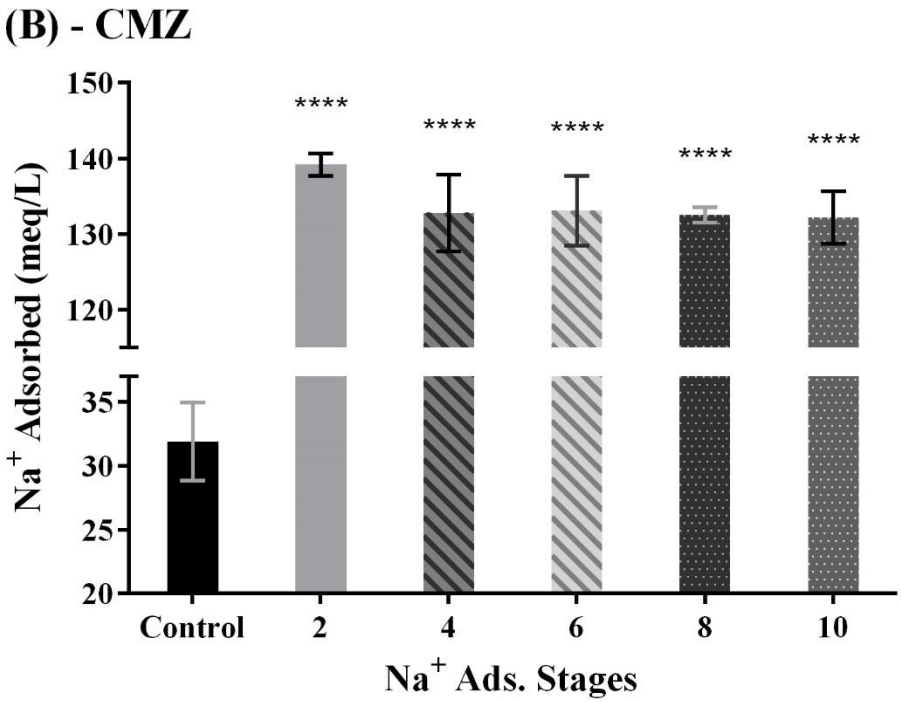
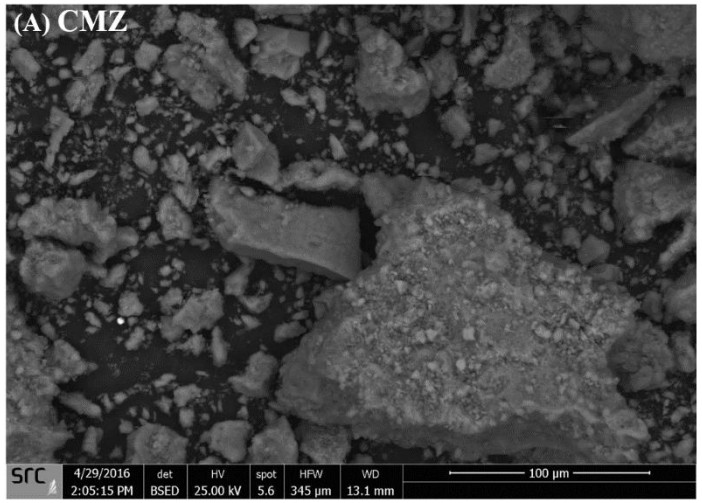
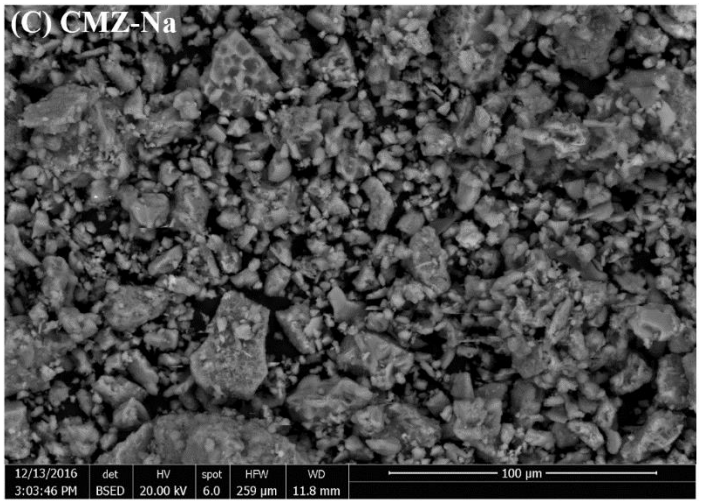


Figure 3.7: Comparison of salinity mitigation from recycled adsorbents and their natural versions which have not undergone pre-treatment or regeneration (control) for BRZ (A) and CMZ (B). Values represent the mean results and standard deviation. The initial sodium concentration was 544 ± 8 meq/L.

The regeneration potential comparison for BRZ and CMZ is graphically depicted in the supplementary data (Figure 3.11) and can be indirectly inferred from Figure 3.6 and Figure 3.7. Natural CMZ adsorbed significantly more Ca^{2+}/Mg^{2+} ions than BRZ; however, the total hardness reduction by Na^{+}–BRZ increased during successive cycles and Na^{+}–BRZ adsorbed more Ca^{2+}/Mg^{2+} ions than Na^{+}–CMZ during the latter stages (significance levels ranging from $0.0001 \leq p \leq 0.01$). The use of a 'hard water' solution was successful at regenerating both zeolites; however adsorption of Na^{+} ions with Ca^{2+}/Mg^{2+}–BRZ decreased during regeneration cycles, thus the adsorbed Na^{+} concentration was significantly less than Ca^{2+}/Mg^{2+}–CMZ ($p \leq 0.0001$).

The influence of pre-treatment and reusing the zeolite for a second adsorption stage was evaluated using SEM images and XRF analysis. Changes in natural CMZ's surface morphology from pre-treatment (Ca^{2+}/Mg^{2+}) (A) and ion exchange (Na^{+}) (B) processes for the first complete cycle, is shown in SEM images in Figure 3.8.





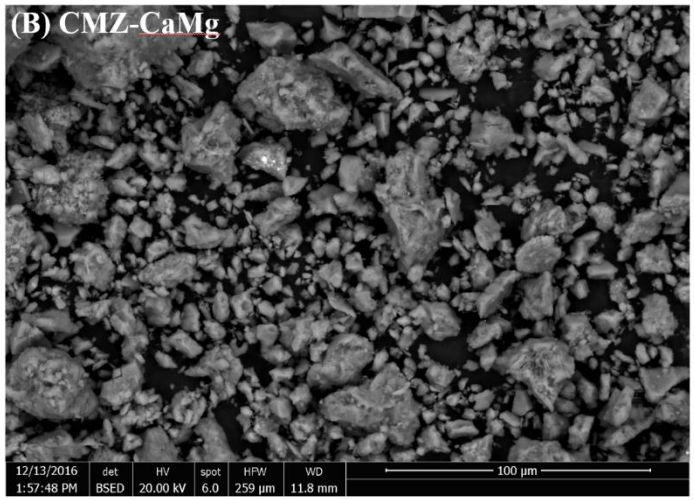


Figure 3.8: SEM images of raw natural CMZ (A) as well as CMZ after ion exchange for water softening (Ca^{2+}/Mg^{2+} –CMZ) (B) and Na^{+} uptake (Na^{+} –CMZ) (C) during the first complete adsorption cycle.

The surface appears to become more irregular throughout the ion exchange reactions in comparison to natural CMZ (A). The SEM images suggest that further changes occurred during the second adsorption stage, Na^+ replacing Ca^{2+} and Mg^{2+} ions, where the zeolite surface appears rougher and highly porous (Figure 3.8 (C)).

XRF analysis of the chemical composition (w/w %) is shown in Table 3.6. The composition relating to Ca^{2+} and Mg^{2+} ions increased, primarily due to the reduction of Na_2O from 3.17 for natural–CMZ to 0.48 for Ca^{2+}/Mg^{2+}–CMZ. XRF results with the second stage of CMZ, Na^+–CMZ, show that Na_2O increased from 0.48 (Ca^{2+}/Mg^{2+}–CMZ) to 3.38. The second adsorption stage with Na^+ removes primarily Ca^{2+} cations; CaO after the first stage was 2.08 and decreased with the release of Ca^{2+} ions from the framework to 0.82. The MgO w/w percentage increased after the first adsorption stage to 0.72 (from 0.38 for natural) and decreased to 0.25 after the Na^+ second stage adsorption. The K_2O composition was also reduced from 3.22 Ca^{2+}/Mg^{2+}–CMZ to 2.75 for Na^+–CMZ, suggesting a small amount of Na^+ exchange with K^+ cations.

Table 3.6: Chemical composition (w/w %) by XRF of natural CMZ as well as after adsorption stages: 1-Ca^{2+}/Mg^{2+} and 2-Na^+.

	Natural–CMZ	Ca^{2+}/Mg^{2+}–CMZ	Na^+–CMZ
SiO_2	72.85	73.13	70.65
Al_2O_3	11.32	11.04	10.24
Fe_2O_3	2.29	2.13	1.99
MgO	0.38	0.72	0.25
CaO	1.32	2.08	0.82
Na_2O	3.17	0.48	3.38
K_2O	3.02	3.22	2.75
TiO_2	0.14	0.14	0.13
MnO	0.01	0.00	0.00
P_2O_5	0.02	0.02	0.02

3.5 Discussion

The selectivity preference for Na^+ and Ca^{2+} ions has been inconsistent in previous studies; therefore, it was important to evaluate both Na^+ and Ca^{2+}/Mg^{2+} as the exchangeable cations used for zeolite pre-treatment. Alkali and alkaline earth metals are relatively inexpensive and commonly available; therefore, they are frequently used to pre-treat ion exchange adsorbents, including zeolite (Gorimbo et al., 2014). Pre-treatment includes introducing a cation to remove pre-existing exchangeable cations from the zeolite surface, prior to adsorption applications, to enhance the cation exchange capacity. The success of pre-treating zeolite is measured by both the adsorption of exchangeable cations and by how easily they can be removed during successive adsorption cycles. Sodium has traditionally been used to pre-treat zeolite because it has been believed to be easily exchanged based on cation selectivity preferences of zeolite (Curkovic et al., 1996; Inglezakis, 2005). The adsorption of Na^+ ions depends on mineral composition, surface area, sodium affinity and pore size, as well as experiment properties (Ganjegunte et al., 2011; Delkash et al., 2015).

Previous studies have used NaCl to pre-treat zeolite for the removal of hard water ions and heavy metals, with increased adsorption suggested mainly due to the selectivity and pre-existing cations. The uptake of Na^+ cations during pre-treatment was more effective by BRZ as compared to CMZ and BRZ(1M), with similar results suggested in Chapter 2 of this study. The exchangeable cations also suggested an abundance order of $Ca^{2+}>K^+>Na^+>Mg^{2+}$ for BRZ, thus, suggesting there was sufficient Ca^{2+} cations for Na^+ to exchange with during pre-treatment. Calcium removal was likely the main exchange mechanism occurring during pre-treatment. Other zeolite properties that may have influenced the superior Na^+ exchange capacity is the enhanced CEC, surface area and mineral content. The effective CEC for BRZ was higher than that measured for CMZ; however, its high exchangeable Ca^{2+} ion content, lowered its direct usefulness for hard water treatment. The pre-treatment zeolites, Na^+–BRZ increased the removal of hardness cations (Ca^{2+}/Mg^{2+}) by approximately 150% when compared to adsorption with natural BRZ. CMZ naturally contains more Na^+ and less Ca^{2+} cations than BRZ, as shown in Table 3.1, resulting in less effective Na^+ uptake during pre-treatment. The Na_2O w/w% XRF data for the natural CMZ and Na^+–CMZ presented in Table 3.6 is approximately equal, suggesting that available exchange sites are close to saturated with Na^+ naturally. Of the Na^+ ions adsorbed to the zeolite framework during pre-

treatment, approximately 7% and 44% of Na^+ cations were removed during Ca^{2+}/Mg^{2+} adsorption, from BRZ and CMZ respectively. These comparisons were created by measuring the Na^+ concentration in the Ca^{2+}/Mg^{2+} sorption solution.

The removal of preferred cations has been known to increase adsorption capacity of other cations (Sprynskyy et al., 2005; Park et al., 2007; Fu et al., 2011). The high Na^+ concentration used in this study would have increased the possibility of desorption of more tightly bound cations, even those cations exhibiting strong interactions with the clinoptilolite, such as K^+ (Xu et al., 2013). The K_2O w/w (%) data presented in Table 3.6 suggests that some K^+ was removed from the zeolite surface during the Na^+ sorption process. The removal of these cations from strong adsorption sites by Na^+ would provide increased available exchange sites and encourage the sorption of hard water cations, exchanging with less tightly bound Na^+ cations.

A sample of BRZ was acid treated using 1M H_2SO_4 (BRZ(1M)) prior to pre-treatment with NaCl. The results outlined in Chapter 2 of this study suggested successful increase in Na^+ adsorption by BRZ(1M) compared to BRZ; however, the adsorbed concentration difference converged as Na^+ concentration increased. Therefore, it was important to evaluate its performance for Na^+ pre-treatment. Results suggest that although Na^+ uptake by BRZ(1M) was higher than CMZ, it was approximately 56% of BRZ and the uptake of hardness ions (Ca^{2+}/Mg^{2+}) after pre-treatment was negligible. These results may suggest at least a partial collapse of the zeolite framework due to acidification. A possible explanation may be dealumination which occurs during acid treatment, where protons attack the Al-O-Si bonds, resulting in the leaching of aluminum ions from the zeolite framework (Christidis et al., 2003). A portion of the aluminum ions reside in tetrahedral sites, thus, extensive removal of Al^{3+} could lead to interlayer disconnection and structural damage of the aluminiosolicate surface; the structural damage weakens the structural framework and causes cracks, defects and vacancies (Liu and Yan, 2000; Jozefaciuk, 2002). Dealumination increases the surface area (surface area of BRZ(1M) was 29 m^2/g higher than BRZ) which was suggested in Chapter 2 to have had a positive effect on Na^+ removal; however, it was likely caused by the destruction of mineral structures in the clinoptilolite framework. Previous studies have suggested that higher silica content zeolites, such as clinotpilolite, should have a stronger acid-resistivity (Rivera et al., 2013; Wang et al., 2016); however, high concentrations of strong acids, such as H_2SO_4, have been suggested to promote structural destruction (Garcia-Basabe et al., 2010;

Salvestrini et al., 2010; Wang et al., 2012). A study conducted by Xiaoyu Wang and associates (2016) used various concentrations of sulfuric acid to treat an Australian clinoptilolite. An analysis of XRD peak intensities suggested acid-treatment with concentrations above 0.1M H_2SO_4 resulted in destruction of the structural crystal phases. The clinoptilolite content changed insignificantly after acid-treatment; however, it has been suggested that structural decomposition is progressive (Salvestrini et al., 2010), thus, continued framework damage likely occurred during successive ion exchange batch tests. The exact cause of the sorption efficiency collapse was not investigated in this study, as the highly acidic conditions created during ion exchange with BRZ(1M), would remain problematic for practical applications. Future studies may evaluate the dual pre-treatment potential using a weaker acid concentration in conjunction with an alkaline metal; however, acidic sorption solution concerns would also need to be addressed.

Every zeolite has a unique framework with cation selectivity based on molecular sieve properties, including number and arrangement of channels, and the cation's size and speciation (Cui et al., 2006; Li et al., 2008). In previous literature, pre-treatment with NaCl is more common than with $CaCl_2$; however, it was important to evaluate the zeolite's selectivity preferences for the cations of interest in this study (Na^+, Ca^{2+} and Mg^{2+}). The selectivity for different cations is influenced by the pore network (size and direction) and active exchange sites, with the zeolite adsorbing cations with a higher affinity preferentially, to the limited number of exchange sites (Delkash et al., 2015). As seen in Figure 3.4 (A) and Table 3.4, the use of Ca^{2+}/Mg^{2+} to pre-treat the CMZ increased the Na^+ adsorption, by approximately 77%. The exchangeable cations originally present on CMZ's framework consist of K^+ and Na^+, limiting the number of active exchange sites naturally available to reduce Na^+ content. Cation selectivity is further affected by physiochemical properties such as valence charge, charge density and hydration energy (Inglezakis et al., 2003; Inglezakis et al., 2004). It has been suggested that the zeolite framework tends to have a higher affinity towards monovalent than divalent cations (Mumpton, 1999; Misaelides, 2011). For cations of the same valence charge, ion selectivity depends on the strength of electrostatic forces and can be predicted by Coulomb's Law (Li et al., 2008); those cations with low hydration energy or small hydrated size (radii) tend to be selectively exchanged by the clinoptilolite as the hydration shell can be removed, allowing the positively charged cation to approach the negative surface sites of the zeolite framework (Cerri et al., 2002; Dyer and Emms, 2005). The removal of Na^+ by Ca^{2+}/Mg^{2+}–BRZ was superior to that of Ca^{2+}/Mg^{2+}–CMZ; a possible explanation includes the

higher Si/Al ratio for BRZ which suggests a low electric field, therefore, a higher affinity of cations with lower electric charge densities, such as monovalent cations than divalent cations (Cerri et al., 2002).

Through the evaluation of both pre-treatment solutions, the regeneration potential of natural zeolite was also studied. The exchangeable cations outlined in Table 3.1 for the natural zeolite samples, suggest the Ca^{2+}-rich BRZ would be less effective for hard water treatment whereas the Na^{+}-rich CMZ was found to be quite unsuccessful for Na^{+} adsorption in Chapter 2. However, as outlined above, using a hard water solution (rich in Ca^{2+} and Mg^{2+} cations) to pre-treat both natural zeolite samples, both the total hardness reduction and Na^{+} adsorption were optimized. The binding forces between the zeolite exchange sites and the cations is considered relatively weak (Gedik and Imamoglu, 2008; Xu et al., 2013), allowing for successive exchange cycles to occur. The integrated treatment process was carried out for five complete sorption cycles. As shown in Figure 3.5, an integrated treatment process using Ca^{2+} and Mg^{2+} hard water and a Na^{+} solution created successive sorption cycles for BRZ and CMZ. The Na^{+} uptake decreased after the first cycle for BRZ and CMZ; however, a stable functioning exchange system was established for both zeolites. Similar functioning systems have been achieved by other authors using different exchangeable cations (Sprynskyy et al., 2005; Öztaş et al., 2008); however, a decreased exchange capacity over successive cycles has also been observed (Huang and Natrajan, 2006). The stable functioning exchange behavior exhibited during the latter cycles suggests that Ca^{2+} and Mg^{2+} are counter ions for Na^{+} exchange.

Throughout the regeneration cycles, the concentration of Na^{+} ions adsorbed by the Ca^{2+}/Mg^{2+}–zeolite was consistently higher than the concentration of Ca^{2+}/Mg^{2+} ions removed during the hard water treatment stages. The initial concentration of the Na^{+} solution (544 meq/L) was significantly higher than the hard water solution (15.3 meq/L as $CaCO_3$). The sorption of the highly concentrated Na^{+} solution suggest Na^{+} ions exchange with both the Ca^{2+}/Mg^{2+} ions and other exchangeable cations present on the zeolite surface. A possible explanation would be the adsorption and desorption of hydrogen ions from the slightly acidic initial solutions. The pH data presented in Figure 3.5(D) suggests H^{+} ions are adsorbed during the hard water treatment stages and released during Na^{+} sorption, allowing for more available exchange sites and decreasing the pH of the sorption solution. The pH increased during both adsorption stages for BRZ (Figure

3.5(C)) compared to the pH of the initial solutions, suggesting uptake of H^+ ions during both stages; this theory can be supported by the increased CEC BRZ possesses, therefore, there are more available exchange sites compared to CMZ. The XRF data presented in Table 3.6 suggests that some K_2O was removed throughout the Na^+ exchange stage; however, it was not a significant ion exchange mechanism throughout the integrated treatment process due to the high selectivity for K^+ ions (Tomić et al., 2012). The primary exchange mechanisms observed during the integrated treatment process would be Ca^{2+}/Mg^{2+} and Na^+, as well as protonic exchange.

The five regeneration cycles conducted in this study suggest a stable functioning ion exchange system has been created with the cations and zeolite exchange sites; however, as the concentrations of cations (Ca^{2+}/Mg^{2+} and Na^+) are not equal, it does suggest that over time, more Na^+ will be adsorbed throughout the successive uptake and removal cycles. As presented in Figure 3.5(A) and Figure 3.5(B), complete adsorption of the Ca^{2+}/Mg^{2+} cations were not achieved, suggesting that the Ca^{2+}/Mg^{2+} ions are adsorbing to all exchange sites available to the particular cations. It has been suggested that the larger hydrated radius, along with steric factors that affect selectivity and diffusion, restrict the mobility of Ca^{2+} and Mg^{2+} cations through the internal zeolite structure more than for Na^+ cations (Inglezakis et al., 2001; Park et al., 2007). Magnesium ions create bulky complexes in water, therefore the hydrate degree limits diffusion through the narrow zeolite pore system (Van Mao et al., 1994; Capasso et al., 2007). The difference also suggests a selectivity preference for Na^+ over Ca^{2+}/Mg^{2+} ions. The clinoptilolite-rich zeolites did not reach their homoionic Na^+ forms; however, future experiments could be undertaken to establish the number of cycles required to reach that state and further study the selectivity relationship between Na^+ and Ca^{2+}. Further research could also include evaluating the influence of competing cations on the integrated treatment system, particularly the influence cations with a stronger affinity, such as the K^+ ions present in potash brine impacted groundwater, would have on the regeneration cycles.

The pre-treatment and regeneration studies conducted on BRZ and CMZ suggest that the exchangeable ions present naturally on zeolite exchange sites influence the adsorption behavior throughout successive cycles (Bolan et al., 2003). Figure 3.6 and Figure 3.7 compared the adsorption of Ca^{2+}/Mg^{2+} and Na^+, respectively, with the cation uptake achieved prior to any pre-treatment (control). BRZ naturally contains high exchangeable Ca^{2+} cations, thus the adsorbed Ca^{2+}/Mg^{2+} ions observed during the first and third stages are lower than successive cycles which

have used Na^+ to create available exchange sites. The evaluation of Na^+ cations by CMZ experienced similar results, as shown in Figure 3.7(B), due to the abundance of Na^+ on natural CMZ exchange sites. Figure 3.7(A) presents a high uptake of Na^+ initially by BRZ before decreasing, suggesting that the second regeneration cycle was unable to remove all of the Na^+ ions present on exchange sites. Sodium removal during successive cycles was reduced likely due to a portion of Na^+ remaining on exchange sites after the first cycle. The selectivity preference, lower hydraulic radius and high initial Na^+ concentration could support this behavior. Further research could be completed to evaluate the direct regenerative capabilities and solidify selectivity results; however, within the scope of this study, the concentrations simulated potential applications. Results suggest consistent Na^+ removal during successive cycles; however it was reduced in comparison to the first cycle. The influence of the abundant cation naturally present on zeolite exchange sites can also be supported by comparing the uptake of Ca^{2+}/Mg^{2+} and Na^+ for BRZ and CMZ. Figure 3.11 in the supplementary data presents a direct comparison of the adsorption potential for BRZ and CMZ throughout the regeneration stages. The uptake of Na^+ cations during the latter treatment cycles is higher for CMZ than for BRZ, suggesting that adsorption is influenced by the dominant cation species on the zeolite's exchange sites naturally (Bolan et al., 2003).

3.6 Conclusion

This study evaluated the adsorption benefits of pre-treating the natural and acid treated clinoptilolites using a hard water solution containing Ca^{2+} and Mg^{2+} cations and a highly saline solution. The solutions were synthetically created to simulate practical applications, including evaluating the hardness of natural groundwater.

Based on previous studies, BRZ, CMZ and BRZ(1M) initially underwent pre-treatment with a highly concentrated Na^+ solution prior to being used for hard water treatment. BRZ adsorbed the most Na^+ initially, followed by BRZ(1M) and CMZ. However, BRZ(1M) removed negligible amounts of hard water cations and was eliminated from further experiments. CMZ initially adsorbed less Na^+ than BRZ, likely due to the natural abundance of Na^+ on its exchange sites; however, it was most effective for hard water treatment. Pre-treatment with a hard water solution (Ca^{2+}/Mg^{2+}) suggested the presence of Ca^{2+} on natural BRZ exchange sites resulted in decreased Ca^{2+}/Mg^{2+} removal; however, increased uptake of Na^+ cations compared to CMZ.

The regeneration potential of BRZ and CMZ was evaluated using an integrated treatment process with Ca^{2+}/Mg^{2+} and Na^{+} sorption stages to create five successive exchange cycles for hard water treatment and salinity reduction. Both zeolite types achieved a stable functioning ion exchange system where the main ion exchange mechanism was the exchange of Ca^{2+}/Mg^{2+} and Na^{+} cations. The integrated treatment system was conducted using synthetic solutions for a limited number of cycles; therefore, future experiments could include evaluating the effects of competing cations and extending the treatment process cycles.

3.7 Supplementary Data

3.7.1 Total Hardness

The Mettler Toledo Titration Application device used the following formula to calculate the total hardness of the sorption solutions:

$$R_1 = \frac{VEQ \times 1000 \times C}{m} \quad (3.12)$$

Where:

- R_1 = calculated total hardness (mg/L as $CaCO_3$)
- VEQ = volume of EDTA consumed to reach equilibrium point (mL)
- m = volume of sample (mL)
- C = calculation function

3.7.2 Zeolite Properties

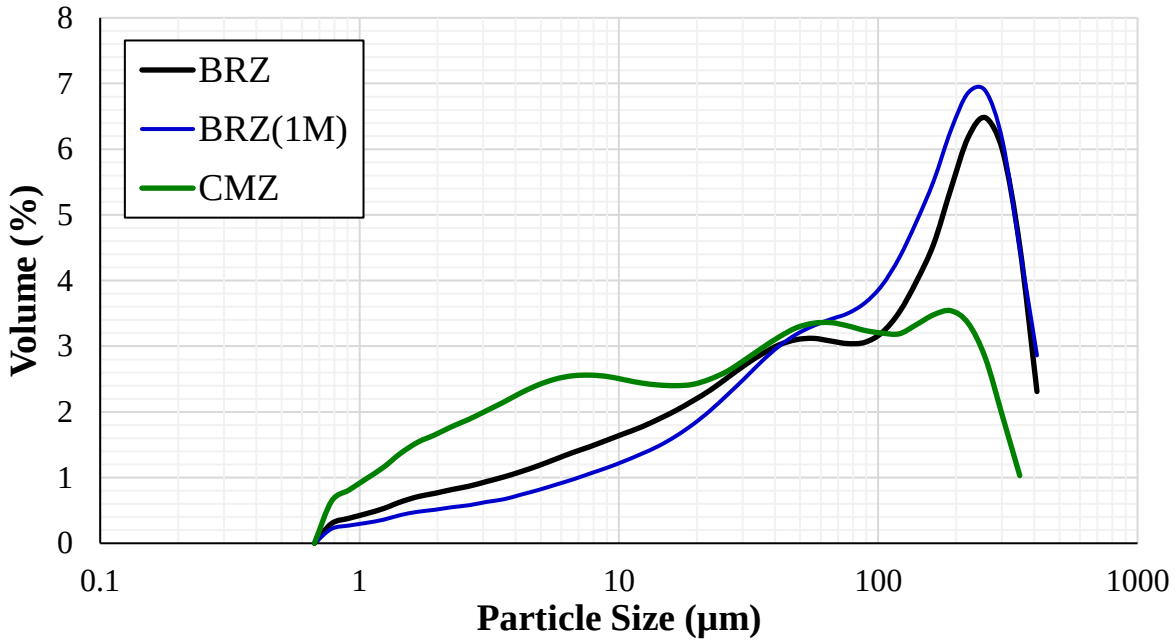


Figure 3.9: Particle size distribution graph for BRZ, BRZ(1M), and CMZ.

Table 3.7: XRD Analysis Results for BRZ, CMZ and BRZ(1M).

Zeolite Sample	Haulandite-Ca (%)	Heulandite-K (%)	Illite (%)	Quartz (%)	Cristobalite (%)
BRZ	61.9	23.7	2.8	2.2	9.4
CMZ	61.6	7.7	19.5	0.5	10.8
BRZ(1M)	74.6	11.5	3.2	2.9	7.7

Table 3.8: XRF chemical composition of the BRZ, CMZ and BRZ(1M) in weight percent for major oxides.

Zeolite	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
BRZ	64.92	8.83	1.90	0.49	2.74	<0.01	3.75	0.28	0.03	0.05
CMZ	72.85	11.32	2.29	0.38	1.32	0.22	3.02	0.14	0.01	0.05
BRZ(1M)	74.33	9.27	2.12	0.51	1.95	<0.01	2.93	0.32	0.04	0.06

3.7.3 Additional Sorption Data

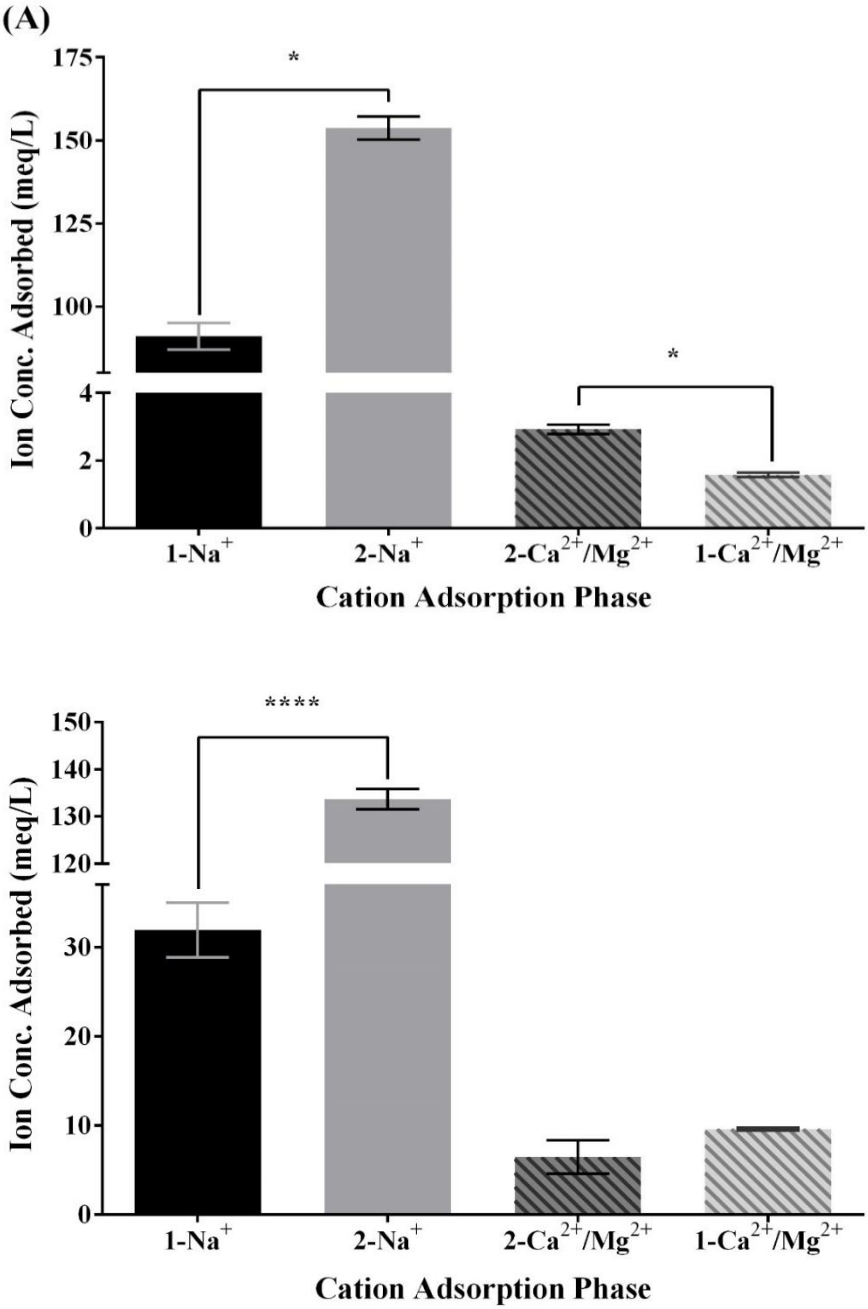


Figure 3.10: Statistical representation of regeneration sorption phases of cations adsorbed for BRZ (A) and CMZ (B) (Table 3.4). Values represent the mean results and standard deviation. Initial synthetic Na^+ and hard water concentrations are 544 ± 8 meq/L Na^+ and 15.3 ± 0.2 meq/L as $CaCO_3$ respectively.

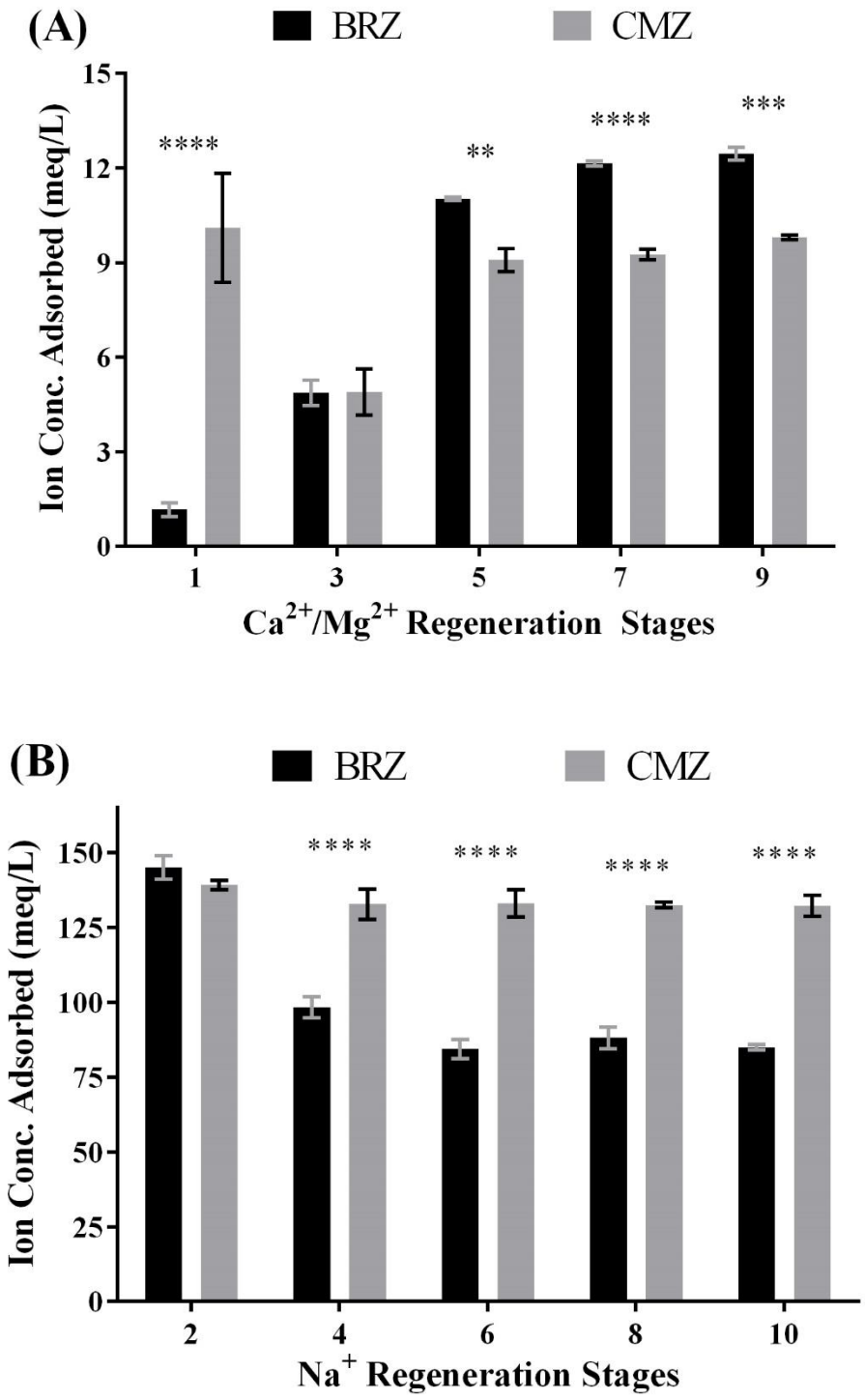


Figure 3.11: Evaluating the performance of regenerated BRZ and CMZ for hard-water softening, Ca^{2+}/Mg^{2+} (A), and salinity mitigation, Na^{+} (B). Values represent the mean results and standard deviation.

4 – Conclusions

4.1 Key Findings

Sodium uptake during sorption experiments was dependent on the initial sodium concentration, solid (zeolite) to liquid (solution) ratio and presence of competing cations. Sodium sorption was also influenced by zeolite characteristics such as exchangeable cations, cation exchange capacity, mineralogical purity and Si/Al ratio. Natural clinoptilolite-rich zeolites from three North American mines were evaluated based on their sodium removal potential and various sorption characteristics. BRZ achieved the highest sodium removal capacity of the natural zeolites, likely due to its high CEC, abundance of calcium naturally present on its exchange sites and mineralogical purity (approximately 85% clintopilolite). BRZ removed approximately 50% more Na^+ ions than CMZ and SCZ, under consistent experimental conditions.

The objective of this study was to evaluate zeolite adsorbents based on their characteristics and sodium sorption capacity. Samples of potash brine solutions and groundwater were mixed to simulate potential practical applications. The PB+GW solution introduced additional cations, primarily K^+, Ca^{2+} and Mg^{2+}, competing with sodium cations for zeolite exchange sites. The presence of additional exchangeable cations reduced BRZ's Na^+ sorption capacity by approximately 10% when compared to synthetic Na^+ solutions. The primary cation of concern would be K^+ as many studies have suggested a preference for K^+ ions on zeolite exchange sites and it is present in potash brine A chemical analysis of the initial and sorption solutions provided insight to the selectivity preferences of the zeolite exchange sites; the suggested selectivity sequence for the clinoptilolite-rich zeolites evaluated in this study was $K^+ > Na^+ > Ca^{2+} = Mg^{2+}$.

Acid treatment technologies were used to strip exchangeable cations and create protonic exchange sites. Acid treatment of natural zeolites increased the surface area, CEC and sodium uptake. Acid treatment increased Na^+ sorption at concentrations below approximately 43.5 meq/L (1,000 mg/L) before gradually converging towards equal sodium uptake at concentrations near 435 meq/L (10,000 mg/L). Acid treatment increased sodium sorption capacity; however, acid treated zeolites were not considered a viable treatment alternative due to the highly acidic sorption solutions resulting from the release of H^+ ions during ion exchange. STXM imagery of the zeolite surface and chemical composition analysis of sorption solutions also suggested dealumination of the

zeolite structure occurred as a result of acid treatment. Acid treated zeolites were eliminated as an adsorbent option for regeneration due to the apparent structural collapse that occurred during pre-treatment with the hard water solution.

A major factor contributing to CMZ's unsuccessful sodium removal was the abundance of sodium naturally present on the ion exchange sites. The outcomes presented in Chapter 2 suggested pre-treating CMZ with a calcium solution would increase its sodium sorption potential. Pre-treatment with a Ca^{2+}/Mg^{2+} solution successfully increased the sodium removal capacity of CMZ by approximately 77%.

An integrated treatment process used simulated hard water (Ca^{2+}/Mg^{2+}) and sodium solutions to evaluate the regeneration potential of BRZ and CMZ. By the end of the five exchange cycles conducted, both zeolites achieved stable functioning exchange systems where the main mechanism for sorption was the Ca^{2+}/Mg^{2+} and Na^{+} exchange. The regeneration cycles increased the sodium removal for CMZ due to the repeated introduction of Ca^{2+} and Mg^{2+} cations to the exchange sites. The exchange sites on BRZ were determined to be naturally calcium rich, therefore, the integrated treatment process introduced Na^{+} repeatedly to increase its water softening potential.

Through studying natural, acid treated, pre-treated and regenerated zeolite forms for their Na^{+} sorption capacity, as well as various properties, potential future applications can choose their zeolite media accordingly. The sorption capacity for Na^{+} among natural zeolites was highest for BRZ, as suggested based on its sorption influencing properties. Since natural zeolites are eco-friendly (the cations exchanged are not harmful), BRZ would be an optimal zeolite for ex-situ or in-situ Na^{+} remediation. Acid treatment increased the Na^{+} sorption capacity; however, the resulting acidic sorption solution suggests a neutralizing agent would be required. Thus, acid treated zeolites would generally only be useable for ex-situ remediation. The abundance of Na^{+} naturally present on CMZ reduced its usefulness as a Na^{+} sorption material; however, pre-treatment and regeneration cycles with a Ca^{2+}/Mg^{2+} solution increased its Na^{+} sorption capacity. CMZ would be a cost effective and useful adsorbent for ex-situ Na^{+} remediation for Saskatchewan potash mines.

4.2 Potential Future Studies

4.2.1 Potential Practical Applications for the Potash Industry

This study characterized each clinoptilolite form based on sorption-influencing properties. These characteristics will be key parameters used to evaluate the optimum clinoptilolite for future experiments. Zeolite is an eco-friendly remediation option that could be incorporated into many different remediation techniques to help treat potash brine impacted solutions. A common practice within the potash industry is to pump impacted groundwater to the tailings pond, likely due to the costs associated with in-situ or ex-situ groundwater treatment techniques. Future experiments could evaluate the effectiveness and practicality of using zeolite as an ex-situ remediation alternative. A filter media containing zeolite could be used to treat potash brine impacted groundwater. Some suggested parameters to study would include the influence of contact time on the sodium adsorption capacity and permeability of zeolite as a filter media.

Another potential use for zeolite within the potash industry is using zeolite to create an in-situ remediation technique such as an impermeable liner. For this alternative, the hydraulic conductivity will be an important parameter for the media chosen. The hydraulic conductivity of BRZ was found to be slightly higher than current Canadian regulation requires to ensure proper containment. Future experiments could build on the research presented in this study by creating zeolite and bentonite mixtures. Experiments would need to determine the optimum mixture of BRZ and bentonite to ensure a sufficiently low hydraulic conductivity, while optimizing the sodium sorption capacity.

4.2.2 Simulating Regeneration Cycles

This study researched regeneration potential through sodium removal and water softening cycles to alternatively remove sodium, and calcium and magnesium cations from solution. Synthetic sodium and hard water solutions were used in batch adsorption experiments with natural zeolites. Future studies could include evaluating the regeneration potential from potash brine impacted groundwater and naturally hard groundwater samples. This would require a complete chemical analysis to understand the influence the presence of additional cations have on the sorption capacity. Based on experiments conducted in Chapter 2, it is assumed that the presence of

potassium ions in potash brine impacted groundwater would impact the exchange potential for both cycles, as zeolite has a high preference for K^+ ions on exchange sites.

It was suggested in this study that homoionic conditions were not achieved throughout the regeneration cycles at either stage. Further experiments could be conducted to evaluate the effects homoionic sodium or calcium conditions have on sorption capacity.

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